

MASS SPECTROMETRIC STUDIES OF GAS PHASE REACTIONS
OF ATOMS AND FREE RADICALS

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by

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This thesis describes work which was carried out in the Department of Chemistry in the University of Canterbury between March 1964 and September 1967. The work is entirely original except where otherwise stated in the text. It was carried out under the supervision of Professor L. F. Phillips and I should like to thank him most sincerely for his advice and encouragement. I am also grateful to Dr M. M. Sutton for helpful discussions and for assistance in the proof-reading of the manuscript.

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Colin G. Freeman

November, 1967

PUBLICATIONS

The following papers relating to the research described in this thesis have been prepared:

1. "The Reaction of Oxygen Atoms with Cl_2O ",
C. G. Freeman and L. F. Phillips, submitted to
Transactions of the Faraday Society, September 1967.
2. "The Reaction of Nitrogen Atoms with Cl_2O ",
C. G. Freeman and L. F. Phillips, submitted to
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3. "The Reaction of Hydrogen Atoms with Cl_2O ",
C. G. Freeman and L. F. Phillips, submitted to
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CHAPTER 1
REVIEW AND INTRODUCTION

1.1 THE HISTORY AND IMPORTANCE OF GAS PHASE REACTIONS OF ATOMS

Gas phase atom reactions, in particular those of hydrogen, nitrogen and oxygen atoms, have long been of interest to research workers in many branches of science. Over 60 years ago, Lewis¹ discovered a golden-yellow afterglow which persisted in a vessel containing nitrogen at low pressures, after an electrical discharge was passed through it. Strutt²⁻⁶ after examining the properties of this glowing gas, and its behaviour when various other substances were added to it, suggested that many of its properties could be attributed to the presence of nitrogen atoms and he named it "active nitrogen". Langmuir⁷ at this time also demonstrated that hydrogen atoms could be obtained by dissociation of molecular hydrogen on a tungsten filament. As with nitrogen, another long-established technique for the production of atoms from molecular hydrogen is the use of an electric discharge in gas at low pressures (0.1 to 1 torr). This method was particularly developed by Wood⁸ and Bonhoeffer⁹⁻¹¹ during the 1920's. Similarly oxygen atoms were produced and direct studies of their reactions with many additives were made in the late 1920's and early 1930's, examples being the work of Geib, Harteck, Kopsch, Rodebush and others¹²⁻¹⁷.

Studies such as those mentioned above produced many important results about the nature of final products of atom reactions, and also the spectroscopic features of reaction

flames, but not very much reliable quantitative kinetic information was forthcoming. The main factors limiting these early workers were the lack of accurate and specific methods for determining absolute concentrations of atoms, and also the inability of early techniques to obtain information about the primary (and usually very rapid) reactions in such systems.

Since about 1950 there has been a great resurgence of interest in the reactions of atoms in the gas phase, and many new experimental techniques have been developed which have now largely overcome the difficulties mentioned above. Some of these will be mentioned later. Most of the impetus for recent work has come from the areas of (1) combustion studies, and (2) upper atmosphere research. In the first of these areas numerous problems had arisen from the attempts to interpret the complicated inter-relationships between hydrodynamics, transport properties and chemical kinetics in a flame or explosion, through measurements of overall processes. Consequently there was a need to obtain reaction rate data involving the atoms and radicals present in flames, but from systems where these species are reacted under simplified conditions. In the second field of research indicated above, it was obvious that in order to fully understand the composition and reactions of the earth's upper atmosphere a knowledge of the photochemistry and reaction kinetics of species present there was necessary. Of particular

importance in this connection are reactions involving oxygen, nitrogen and hydrogen atoms; oxygen and nitrogen molecules; ozone; nitric oxide and nitrogen dioxide; and hydroxyl radicals as well as other minor atmospheric constituents.

1.2 METHODS USED IN ATOM REACTION STUDIES

Some of the more commonly used methods now employed for the investigation of gaseous atom reactions in the laboratory include:

(1) Flash photolysis: Porter, Norrish and coworkers¹⁸⁻²⁰ are particularly associated with the development of this technique. Reactant gas mixtures are subjected to a high intensity photolytic flash of a few microseconds duration and absorption spectra are then recorded at various time intervals after flashing. Thus the progress of the reactions of the atoms and radicals formed initially are followed and kinetic information and also data about excited product species are deduced. Examples of such studies are the decompositions of nitrogen dioxide, chlorine dioxide²¹ and chlorine monoxide²².

(2) Shock tubes: When a gas is subjected to a shock wave in a tube it undergoes a homogeneous, and virtually instantaneous, temperature rise which is typically of the order of several thousands of degrees Kelvin. This usually causes the gas to dissociate to atoms and/or radicals which then may undergo secondary reactions. By using techniques such as

absorption spectroscopy or, more recently, analysis by a time of flight mass spectrometer, the changes in the gas are monitored. The method has been used to measure, for example, dissociation rates of many diatomic gases and hence rates for the reverse processes (i.e. the recombination of atoms) are derived. The unique advantage of the method is the wide range of temperatures accessible (6000°K and greater). The subject has been reviewed by Bradley^{23,24}.

(3) Explosion limits: The explosion limits for the thermal reaction of hydrogen and oxygen are controlled by the rates of reactions involving hydrogen atoms. The effect of various molecules, such as hydrocarbons, on the explosion limits may be used to determine their reaction rates with hydrogen atoms. The method has been reviewed by Voevodskii and Kondratiev²⁵ and gives consistent rate constants providing the mechanism can be analysed, although it is applicable over only a small temperature range.

(4) Photolysis methods: A variety of photochemical techniques have been used in studies of atom reactions. The use of vacuum ultra violet light sources to give direct production of atoms by dissociation of suitable molecules has been described by McNesby and Okabe²⁶. Decomposition may also be effected indirectly as is the case in the mercury-sensitized decompositions of hydrogen and nitrous oxide to yield hydrogen atoms and oxygen atoms respectively; this method has been reviewed by Cvetanovic²⁷. More recently

techniques have been developed for studying the reactions of electronically excited atoms, either by using vacuum ultra violet radiation of sufficiently high energy, or by direct excitation of ground state atoms, e.g. use of Lyman- α radiation to excite ground state hydrogen atoms^{28,29}.

(5) Flame studies: Premixed flame studies have been carried out using, for example, hydrogen-oxygen or hydrocarbon-oxygen mixtures. The concentrations of atoms, radicals and molecules present are normally followed photometrically or mass spectrometrically and kinetic information has been deduced for many of the atom reactions which occur within such flames, and with various trace additives. Most of these studies yield information in the temperature range 1000° to 2000°K^{30,31}.

(6) Discharge-flow studies: Probably the most widely used system for studying gas phase reactions of atoms has been the discharge-flow tube. Since the early experiments of Wood, Bonhoeffer, Harteck and others⁸⁻¹⁵ many new experimental techniques have been applied to studies in flow tubes and the most important of these will be reviewed below.

1.3 DISCHARGE-FLOW SYSTEMS

(i) General Features

The essential feature of a discharge-flow system is that reactant gases are pumped continuously through a tube at low total pressures, typically 0.1 to 10 torr. Atoms are

produced by some form of discharge through a portion of the gas and other reactants are added downstream, subsequent reactions being monitored by a variety of methods.

To produce atoms the earliest workers in this field used either a discharge between metal electrodes within the flow tube, or pyrolysis of gas over a hot filament. Most systems now incorporate electrodeless microwave or radio-frequency discharges³² which avoid contamination from the electrodes and can be used over a wider pressure range. Typically a few percent of a diatomic gas is dissociated by such a discharge, although the extent of dissociation may be increased if an excess of an inert gas carrier is used.

The main requirement for kinetic studies in a discharge-flow system is an accurate and specific means of determining atom and free radical concentrations, and in addition, some means of following the consumption of other reactants and the appearance of products. It is true to say that the large increase in the use of these systems over the last decade has been almost entirely due to the development of new methods of measuring atom concentrations.

(ii) Estimation of Atom Concentrations

The earliest method developed involved the use of the catalytic probe¹⁵. The probe consists of a wire, coil or foil which is inserted into the gaseous stream. Determination of the heat evolved when reactive species recombine on the highly catalytic surface gives a measure of the atomic

concentration. Although this technique has been improved it suffers from the obvious disadvantage that it is unable to differentiate between different atoms or radicals present, nor between these and excited molecules. Since the latter are often present in appreciable amounts, erroneously large heats are produced.

Wrede-Harteck gauges^{33,34} have also been in use for nearly forty years. These depend on the steady state pressure difference which is established when the atoms and molecules being studied effuse through a small hole on to a catalyst where the atoms recombine and only the molecules effuse back into the system. Again these are non-specific towards different atoms and they are limited to low pressures.

Chemiluminescent methods are highly specific towards individual atoms. These consist of measuring the intensities of characteristic emissions produced by excited species formed by the interaction of atoms with each other or with additives. For example, the yellow nitrogen afterglow is proportional to $(N)^2$ ³⁵, HNO emission from $H + NO$ is proportional to $(H)(NO)$ ³⁶, and the air afterglow from $O + NO$ is proportional to $(O)(NO)$ ³⁷. The main limitation of these methods is that the constants of proportionality between emission intensities and absolute atom concentrations need to be determined independently. Emission from excited product species may also be monitored photometrically to provide kinetic information.

Absorption spectroscopy has been used to measure concentrations of hydrogen, nitrogen and oxygen atoms³⁸, but the principal disadvantage lies in the fact that the absorption spectra of these species all lie in the vacuum ultra violet region where experiments are difficult to perform. The method is probably more suited for measurement of free radical concentrations and is also used to follow concentrations of other reactants, intermediates and products in flow systems.

Electron spin resonance provides a very sensitive and specific method of detecting free atoms. There are however considerable calibration problems but these have been studied³⁹ and the method has been used to obtain accurate measurements of atom concentrations^{40,41}. Kinetic studies of atom reactions have recently been carried out using this technique. The main disadvantages of this application are the complexity and cost of the equipment, and the fact that in order to obtain sufficient resonance a considerable length of flow tube has to be used. Therefore only an average value of atom concentration over an appreciable tube length is obtained.

Gaseous titrations are probably the most popular methods currently used for estimating atom concentrations. The requirement of a suitable titrant gas is that it reacts rapidly with the particular atom in question, and further that it reacts in a manner which is well understood, particularly as to the overall reaction stoichiometry. Thus for example,

nitric oxide is used to determine nitrogen atoms, nitrogen dioxide to estimate hydrogen or oxygen atoms, and nitrosyl chloride for chlorine atoms.* Titration "end points" are normally determined photometrically or mass spectrometrically.

Mass spectrometry, in addition to finding application in titration methods, has also been used to observe atoms directly in flow systems. Atoms and free radicals have ionization potentials below the corresponding appearance potentials for their ions from parent molecules. Thus if low energy electrons are used in the ionization chamber of the mass spectrometer, atoms or radicals may be detected directly. A further requirement is some form of sampling system to the mass spectrometer which minimizes the probability of reactive species recombining through wall collisions before entering the ionizing region. Foner and Hudson^{42,43} have described a molecular beam sampling system which they have used to detect hydrogen atoms, oxygen atoms, hydroxyl radicals and the HO_2 radical in hydrogen/oxygen flames. Another example is the work of Herron⁴⁴ who has observed nitrogen atoms and hydrogen atoms directly in the reaction of nitrogen atoms with ethylene. Calibration of such measurements to give absolute atom concentrations is required however and this is usually done by gas titration. (Further applications of mass spectrometry to discharge-flow reactions will be described in section 1.4.)

*For fuller description of these titration methods see section 2.5(ii).

(iii) Limitations of Fast Flow Systems

Some of the limitations in the use of fast flow systems in kinetic studies of reactions have been discussed by Kaufman⁴⁵. The full mathematical description of flows of discharged gases through cylindrical tubes is extremely complex when volume and surface recombination, radical and axial diffusion, and the viscous pressure drop are all taken into account. It may be shown however that for flow velocities of around 5 to 10 metres/second, with total pressures of 0.1 to 0.2 torr, and with walls poisoned against surface atom recombination (i.e. conditions which will later be shown to be those prevailing in the present study) that the effects of recombination and diffusion are almost negligible. By far the most important source of error is that due to viscous pressure drop along the tube.

Using the simple Poiseuille flow expression

$$p_2^2 - p_1^2 = \frac{16FlhRT}{r^4\pi}$$

and inserting appropriate values of the constants for argon, oxygen or nitrogen at room temperature, the expression reduces to

$$\Delta p = 1.2 \times 10^{-6} \frac{v}{r^2} \times l ,$$

where Δp is the pressure drop in torr, v is the average linear gas velocity in $\text{cm} \cdot \text{sec}^{-1}$ at room temperature, and r and l are the tube radius and length in cm. Thus for flows such as that quoted above the pressure drop is about 1 to 2×10^{-3} torr per cm of tube length, which represents about 1% pressure change per cm.

1.4 MASS SPECTROMETRIC STUDIES OF ATOM REACTIONS

Mass spectrometry provides an extremely powerful tool for analysis of gas mixtures in that it is capable of detecting very low partial pressures - typically only 10^{-5} to 10^{-7} torr of gas sample being required for analysis. Furthermore it has the ability to detect free radicals and atoms as well as stable molecules in reacting mixtures. It is not confined to species having strong absorption or emission in an accessible wavelength region as are spectroscopic methods, or to free radicals as is the case with electron spin resonance. There is one major limitation in the use of a mass spectrometer to study chemical reaction kinetics and the short-lived intermediates present during reactions. This is the requirement that samples for analysis must be taken when the reaction is proceeding very rapidly and the analysis performed before further reaction can take place. There are two approaches to this problem, both of which have been successfully applied to the study of gas phase atom reactions.

The first method is to perform very rapid static analyses. Such studies have been carried out to follow the kinetics of fast discontinuous reactions in flash photolyses⁴⁶, "cold" flames⁴⁷, and shock tubes^{48,49}. These workers normally use time-of-flight instruments which are able in some cases⁴⁹ to scan the required mass spectrum every 25 microseconds. Alternatively oscillographic display of the

output from the secondary electron multiplier may be used.

A more common approach however is to use a conventional mass spectrometer with continuous sampling from a fast flow reaction system into the ion source. The distance travelled by the reactant gases from the point of mixing to the sampling leak of the mass spectrometer can be related to the reaction time and thus by varying the reaction distance kinetics can be followed. It may be noted that in both this and the previously mentioned type of studies there is normally a pressure drop of at least several orders of magnitude when the gas sample enters the ion source. As a result even the most rapidly occurring reactions will be virtually "frozen" during the additional time required for mass spectral analysis.

The earliest mass spectrometric studies of free radicals in flow tubes were reported by Eltenton⁵⁰, who observed many radicals in the thermal decomposition of organic compounds and in low pressure flames. Lossing and co-workers⁵¹ made extensive use of the flow technique to study the kinetic behaviour of free radicals which they also produced by thermal decomposition of organic compounds. This method was next extended to the study of reactions of oxygen, nitrogen and hydrogen atoms in conventional flow-discharge systems, notably by Kistiakowsky and Schiff and their respective associates. Jackson and Schiff⁵² studied the mass spectrometry of active nitrogen and were able to show that it contained nitrogen atoms in the 4S ground state. Herron and Schiff⁵³ made a similar

study of discharged oxygen and showed that ^3P ground state oxygen atoms as well as excited oxygen molecules were present. These workers also obtained some preliminary information about the rates of reactions of oxygen atoms with nitrogen oxides. Berkowitz, Chupka and Kistiakowsky³⁵ confirmed the results of Jackson and Schiff and also showed that the intensity of the nitrogen afterglow was proportional to the square of the nitrogen atom concentration. Kistiakowsky and Volpi⁵⁴ describe the use of a stirred reactor, in a fast-flow system, in which they studied reactions of nitrogen and oxygen atoms with nitrogen oxides using a mass spectrometer to measure steady-state concentrations. With this type of reaction vessel only the rates of relatively slow bimolecular reactions were measurable with any degree of accuracy. Phillips and Schiff⁵⁵⁻⁵⁹ used the type of reaction system, with a movable inlet jet in a linear flow tube, which will be described more fully in Chapter 2. With this apparatus these workers measured rate constants for a number of reactions of nitrogen atoms, oxygen atoms and hydrogen atoms with nitrogen oxides and ozone. The system has been shown to have the ability to study even the most rapid atom reactions known, for example, the reactions of hydrogen atoms with nitrogen dioxide and ozone⁵⁸, and that of nitrogen atoms with nitric oxide⁵⁵. In the last few years this type of system has come into fairly general use in flow-discharge kinetic studies and has been applied by a number of groups of workers to a variety

of atom reactions. The most notable studies have been carried out by Phillips, Schiff, Harteck, Herron, Dunford, Volpi, Lambert and their respective associates.

More recently, Ferguson et al⁶⁰ have been successful in applying essentially the same technique, using a fast-flow system and a quadropole mass spectrometer, to the study of kinetics of ion-molecule reactions, particularly those of probable importance in the earth's ionosphere. Many of these processes have been found to have rate constants one or two orders of magnitude greater than any known atom reactions.

1.5 GAS PHASE PROPERTIES OF REACTIONS OF Cl(I) and Cl(II) OXIDES

(i) Chlorine Monoxide

Chlorine monoxide (Cl_2O) has long been known to be unstable under the influence of heat or light, the decomposition processes leading to chlorine and oxygen as products. The instability and reactivity of this substance are such that explosions are observed upon heating or sparking the gas, particularly when air (or oxygen) is present; upon boiling the liquid, if care is not taken; when the gas is brought into contact with rubber, cork, or other organic materials; or even upon impact.

The thermal decomposition of chlorine monoxide is an interesting problem in kinetics which has been the subject

of much investigation. Although the process is explosive if heat is applied rapidly or locally, under carefully controlled temperature conditions it will proceed at a conveniently measurable rate between 60° and 140°C . The reaction has been shown to be homogeneous, and after a slow induction period it proceeds at an accelerating rate, often culminating in an explosion. No certain mechanism has been determined, but the reaction has been interpreted as a chain process which has a bimolecular initiation step, involving two Cl_2O molecules, and in which Cl atoms and ClO radicals act as chain carriers^{61,62}. Szabo⁶³ has applied his four-stage mechanism of chain reactions to this system using the data of other workers. No kinetic information about individual and specified steps in the reaction has been forthcoming however.

The photochemical decomposition of chlorine monoxide has also been the subject of a number of investigations. Bowen⁶⁴ and Bodenstein⁶⁵ both observed that two molecules of Cl_2O were decomposed by each quantum absorbed with light of 4050 to 4600 \AA . Finkelnberg et al⁶⁶ used light of 3130 to 4360 \AA and observed a quantum yield of 3.5 with less than 10% variation between wavelength extremes, while Schumacher and Townend⁶⁷ used light of 2350 to 2750 \AA and observed a quantum yield of 4.5. The visible and ultra-violet absorption spectrum of Cl_2O has been studied^{66,68}, and shows continuous absorption below 6600 \AA which corresponds to the

onset of the process



There are maxima in the spectrum at 5300Å and 4100Å which correspond to the above dissociation process producing excited chlorine atoms. Another maximum at 2560Å corresponds to



This process is energetically possible below 3060Å²².

The quantum yields obtained by different workers, and also the observation that small amounts of ClO_2 are formed during the decomposition process may be explained if the chlorine atoms and oxygen atoms, resulting from the primary photochemical processes, are each capable of reacting rapidly with a further Cl_2O molecule. The ClO radicals which are formed in these rapid processes, as well as in the initial decomposition step, are capable either of recombining with each other, yielding oxygen and chlorine molecules, or of attacking further Cl_2O molecules. The relative importance of these processes will depend on the pressure and conditions of the reaction and therefore the differing results for quantum yield can be explained. Probably the most important of the other chain terminating processes is the recombination of chlorine atoms either in the presence of a third body or at the wall. It has been observed that in the liquid phase photochemical decomposition of Cl_2O in carbon tetrachloride quantum yields are much lower. In this case

the reactions $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$ and $\text{Cl} + \text{ClO} \rightarrow \text{Cl}_2\text{O}$ occur more frequently than in the gas phase and therefore compete with Cl_2O molecules for chlorine atoms.

(ii) Hypochlorous Acid

Hypochlorous acid (HOCl) is known as a rather unstable acid which cannot be prepared in concentrated form and which decomposes even in aqueous solution upon standing, hydrochloric and chloric acids being the products. Distillation of the acid solution yields some HOCl in the gaseous molecular form although equilibrium will be set up with water vapour and chlorine monoxide (the anhydride of the acid). An absorption spectrum has been observed for HOCl vapour in the region 2400 to 4000Å⁶⁹. The gaseous acid has also been observed in the thermal decomposition of perchloric acid⁷⁰, as a product in the thermal reaction of Cl_2O and propane⁷¹, and it is almost certainly present during the photochemical reaction of Cl_2O and hydrogen^{71,72}. Hypochlorous acid has not however been prepared in pure gaseous form and virtually nothing appears to be known of its reactions and reaction kinetics in the gas phase.

(iii) ClO Radical

Chlorine (II) oxide is not a well characterized stable compound. As has been mentioned previously however, the free radical species ClO features prominently in the thermal

and photochemical decompositions of chlorine monoxide. This radical is also known to be important in the decomposition of chlorine dioxide, which is readily dissociated photochemically by the process



this being followed by a chain reaction. The ClO radical is also important as an intermediate in a number of other reaction systems. Iredale and Edwards⁷² showed that in the photoreaction of hydrogen with Cl₂O the ClO radical was a more important chain carrier than hydrogen atoms. Phillips and Shaw⁷¹ examined the reaction of Cl₂O with propane and showed that ClO radicals (and not chlorine atoms) were the main chlorinating species, and that iso-propyl chloride and not n-propyl chloride was the favoured product, the ratio of the two compounds in the products being 7.2 to 1. Other systems where the ClO radical is present as an intermediate include the chlorine sensitized decomposition of ozone⁷³, the reaction of Cl₂O with NO₂⁷⁴, and many other reaction flames where oxygen atoms or chlorine atoms are present with chlorine or oxygen containing compounds respectively. The band-spectrum of ClO in the visible and ultra-violet has been observed in emission in hydrogen-oxygen flames with chlorine present^{75,76}, and more recently in the reaction of oxygen atoms with methyl chloride⁷⁷. Absorption spectra have been observed in the flash photolyses of chlorine-oxygen mixtures^{78,79}, chlorine monoxide²², and chlorine dioxide²¹, to quote just a few examples. An

electron spin resonance spectrum was also reported recently for the ClO radicals in a discharged chlorine-oxygen mixture⁸⁰.

(iv) Thermochemistry

Thermochemical data for Cl₂O, HOCl and ClO, as listed in the JANAF tables⁸¹, have been obtained from the following sources.

The heat of formation of Cl₂O cannot be measured directly since in common with other chlorine oxides this compound is endothermic. The value is calculated therefore by application of Hess' law to ΔH values for a number of other processes. Evans et al⁸² have surveyed the literature extensively and have calculated ΔH_f° at 298°K for Cl₂O(g) by two separate paths as 18.08 and 18.3 kcal.mole⁻¹. They quote their "best" value as 18.1 ± 0.3 kcal.mole⁻¹.

It has been pointed out that little is known of the properties of gaseous HOCl and as a result the heat of formation listed for this compound is only an estimated value. The heat of formation for HOCl(aq) is calculated from other related thermochemical data. The heats of solution of other weak acids in water are considered and the heat of solution for HOCl is then estimated as -8 ± 3 kcal. This leads to a value for ΔH_f° at 298°K for HOCl(g) of -23 ± 3 kcal.mole⁻¹. In addition the ΔH_f° values of H₂O(g) and Cl₂O(g) are averaged to give a value for HOCl(g) of -20 ± 5 kcal.mole⁻¹. The final estimate is then quoted as -22 ± 3 kcal.mole⁻¹.

The dissociation energy of $\text{ClO}_{(g)}$ has been obtained spectroscopically (from the convergence of bands) by Ramsay and co-workers^{83,84}. From this value ΔH_f° at 298°K for $\text{ClO}_{(g)}$ is calculated and is listed as $24.19 \pm 0.05 \text{ kcal.mole}^{-1}$.

1.6 INTRODUCTION TO THE PRESENT STUDY

In this work a mass spectrometer was used to monitor reactant concentrations in a fast discharge-flow system. The reactions of chlorine monoxide (Cl_2O) with oxygen atoms, hydrogen atoms and nitrogen atoms were studied. The mass spectrometer was sufficiently sensitive for very low reactant concentrations to be used, and thus values were obtained for the rate constants of each of the rapid primary atom reactions. In addition, the overall stoichiometry of each of the reactions was determined, and products and intermediates identified.

Although the decompositions of the chlorine oxides have been extensively studied, virtually all of the quantitative kinetic information on these systems has come from the flash photolyses of chlorine/oxygen mixtures^{78,79}, chlorine monoxide²², and chlorine dioxide²¹, and from photometric measurements on discharge-flow systems⁸⁵⁻⁸⁸. These experiments have yielded much valuable kinetic information about the behaviour of intermediates such as the ClO radical and the nature of the slower secondary processes occurring. These systems have not however permitted measurements of the rates of very fast primary reactions. The reactions of

atomic oxygen with Cl_2O and ClO are examples of such fast processes and kinetic information about these reactions should be of importance in further understanding the mechanisms of chlorine oxide decompositions.

Reactions in the atomic hydrogen/chlorine monoxide system are of some interest in connection with the use of perchlorate oxidizers in rocket fuels. The only previous kinetic study involving Cl_2O and hydrogen appears to be the work of Iredale and Edwards⁷² on the photoreaction of Cl_2O with H_2 .

The reaction of atomic nitrogen with chlorine monoxide might be expected to be qualitatively similar to the reactions of atomic nitrogen with halogens^{89,90}. It is also likely that in this system the NCl radical will be an important intermediate, as well as the ClO radical. Spectra of NCl have been observed by Briggs and Norrish⁹¹ in the flash photolysis of gaseous NCl_3 , and by Milligan and Jacox⁹² as a product of the photolysis of ClN_3 in a solid matrix. The reactions of NCl appear to be largely unknown.

CHAPTER 2

EXPERIMENTAL APPARATUS AND TECHNIQUES

2.1 REACTION SYSTEM

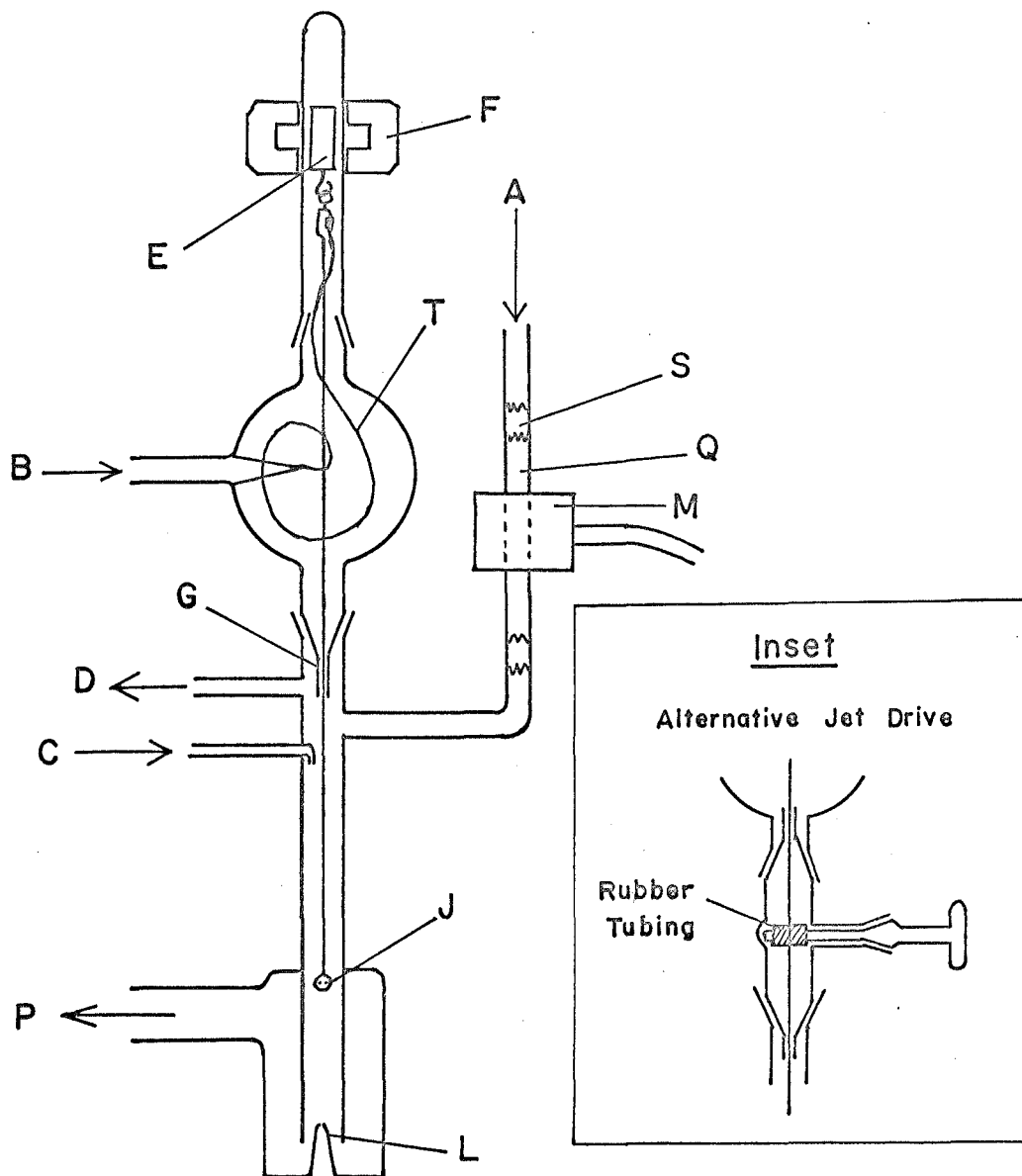
The essential features of the fast flow reaction system are shown in Figure 1.

One of the reactants entered the 17 mm i.d. pyrex reaction tube via a 13 mm o.d. tube A. Atoms were formed by partial dissociation of a diatomic gas as it passed through an electrodeless discharge, which was sustained in the quartz section Q of the tube by a microwave cavity M. The microwave power was provided by a "Raytheon" 125 watt diathermy unit operating at 2450 Mc/sec. In all experiments the microwave output was operated in the range 12 to 60 watts, and the partial pressure of atoms formed was never greater than about 3% of the total pressure. It has been shown that atoms produced in this way are almost exclusively in their ground states^{52,53} and this was assumed to be the case in the present work. The discharge region was separated from the reaction tube by two right-angled bends in order to avoid photolysis of reactants by radiation from the discharge.

The second reactant was introduced at B, passed through a length of flexible p.v.c. tubing T, and then entered the reaction vessel by way of an axial 3 mm o.d. tube, terminating in a 4.5 mm diameter, 6-hole, spherical inlet jet J. This jet could be moved over a 30 cm length of the flow tube.

FIGURE 1

The Reaction System (schematic)



- | | | | |
|---|--|---|------------------------|
| A | Diatomic Gas Inlet | Q | Quartz section of tube |
| B | Reactant Inlet (Cl_2O) | M | Microwave Cavity |
| C | Titrant Gas Inlet | S | Graded Seal |
| D | Micromanometer Inlet | T | P.V.C. Tubing |
| E | Soft Iron Slug | J | Moveable Inlet Jet |
| F | Magnets | L | Sampling Leak |
| G | Guide Sleeve | P | Outlet Pump |

Thus the time available for reaction before gases reached the mass spectrometer sampling leak L was variable. It was found that the most successful method of moving the jet was to use an external magnet F. The magnet was mounted on guide rails and moved a soft iron slug E within the reaction system. This iron slug was previously coated with a solution of sodium silicate and sodium phosphate, baked dry, and then attached to the movable inlet jet in the reaction system. The purpose of the coating was to protect the iron from corrosion and to provide a surface similar to phosphoric acid poisoned pyrex. The guide sleeve G ensured a central position of the jet within the reaction tube. Alternatively the tube could be moved by rotation of a rubber-covered rod pressed against it (see inset of Figure 1). It was found however that this arrangement was less reliable than the magnetic version. The principal source of trouble arose from the gradual accumulation, on the rubber, of a film of grease which caused friction to be lost.

A fixed inlet jet C, 35 cm from the sampling leak, was used to introduce NO and NO₂ for titration of atom concentrations.

Pressures in the reaction tube were measured by means of a Consolidated micromanometer at D. The pressure range of this instrument was from 0 to 500 microns, with an accuracy of 0.1 micron (1 micron = 10^{-3} torr).

The flow tube was evacuated with a Heraeus Roots R150 pump ($1500 \text{ litres} \cdot \text{minute}^{-1}$) which was backed by a Welch model 1397 2-stage rotary pump. After leaving the flow tube by exit P, the gases passed through a large bore trap, a cold trap at -78°C , and thence to the pumps. With both pumps operating linear flow velocities in the reaction tube were between 11 and 14 $\text{metres} \cdot \text{sec}^{-1}$ in the pressure range 0.1 to 0.2 torr. With the Roots pump turned off velocities of about 3 $\text{metres} \cdot \text{sec}^{-1}$ were attained at pressures of around 0.2 to 0.3 torr.

The mass flows of stable reactants were measured by means of capillary flowmeters, and the flow rates of all reactants were controlled by Edwards stainless steel needle valves.

A small central portion of the gas stream was continuously sampled into the mass spectrometer through the leak L. Sampling leaks were prepared by sparking a hole of approximately 20 microns diameter in the end of a pyrex thimble, the wall of which was blown to thickness of between 20 and 50 microns. The circuit used for making such holes is shown in Figure 2. When the condenser had charged to 300 volts the switch was depressed and a spark produced between the tips of two needles N_1 and N_2 . The tip of one needle was placed on the inside and the other on the outside of the thimble end. The spark was directed to the centre of the thimble by a coating of wax with a small hole scratched in

FIGURE 2

Circuit used for making Sampling Leaks

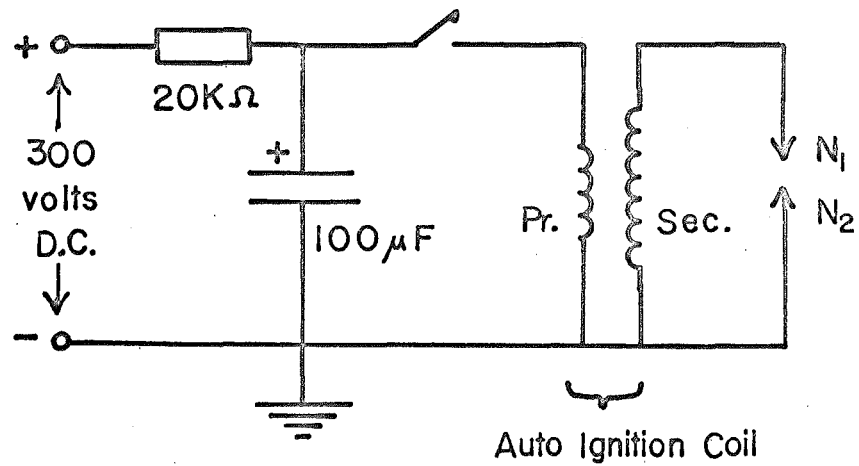
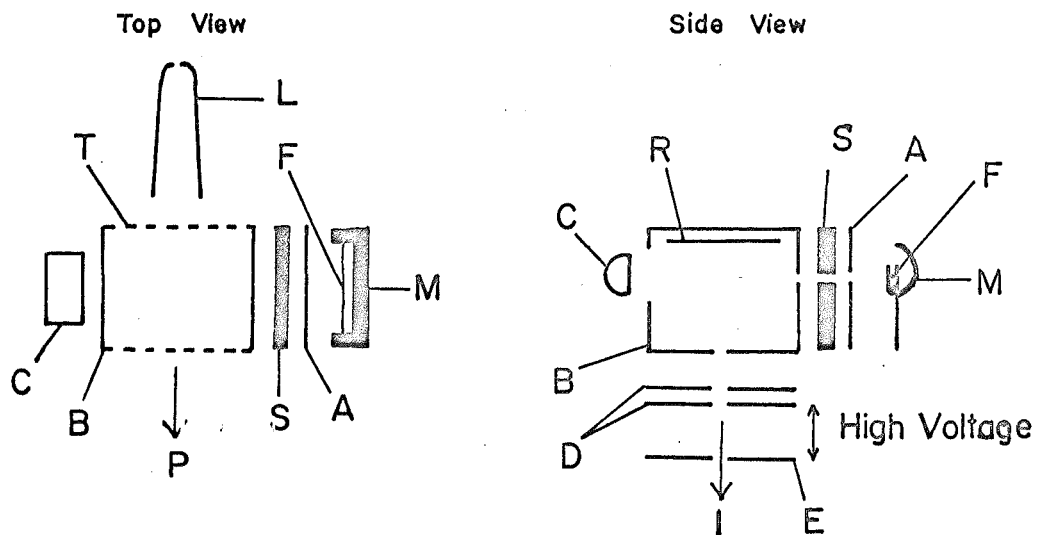


FIGURE 3

Mass Spectrometer Ion Source (schematic)



L Sampling Leak
T Tungsten Mesh
F Filament
C Collector

B Ion Box
P To Pump
S Electron Collimator
A Anode
M Filament Mount

R Ion Repeller
D Ion Focus Plates
I Ion Beam
E Earth Plate

the desired spot. The criterion for a suitable leak was that it was centrally placed on the end of the thimble, that it was able to withstand a pressure difference up to 1 atmosphere, and that it was of suitable size (the diameter was calculated from the measured molecular flow through the leak). Small leaks were enlarged by gentle sparking with a Tesla coil. With a correctly sized leak in place, a pressure of about 10^{-1} torr in the reaction system produced a pressure in the mass spectrometer ion chamber of 10^{-5} torr.

In most experiments the walls of the reaction tube were coated with 10% orthophosphoric acid in order to minimize recombination of atoms in the system⁹³.

2.2 MASS SPECTROMETER

The mass spectrometer which was used for analysis of reactant gases in this work, was assembled by Professor L.F. Phillips of this department during 1963 and is essentially the same as that used by Phillips and Schiff⁵⁵ in Montreal.

The spectrometer was a single order, direction-focussing instrument having a 90° , 6-inch radius, magnetic analyser. The ion accelerating voltage was operated at a constant value, usually 1500, 2000 or 2500 volts, and an electromagnet was used to scan the mass spectrum. The magnet current could be varied either manually or automatically.

The instrument was able to scan the mass range 1 to 150 and possessed a resolving power of about 1 in 100.

Although this resolution is relatively low it is of advantage in the present study since it was desired to keep a chosen mass spectral peak in focus over a long period of time.

If the resolution were higher then more stringent limits would be placed upon the quality of power supplies required in the instrument. Another reason why low resolving power was required was the fact that only relatively small molecules are used in this work.

The mass spectrometer ion source was of the electron bombardment type. The electron gun was similar to that used by Cloutier and Schiff⁹⁴ for their retarding potential difference method of determining appearance potentials. A schematic diagram of the present electron gun is given in Figure 3. The electron gun could be operated as a pulsed ion source if desired, although this was not done in the present study. A double square-wave generator can receive the 30 kc output from an oscillator and convert it to two out-of-phase square waves of amplitude 20 volts peak to peak⁹⁵. One pulse can turn off the electron gun while the other repels electrons from the ion chamber. During the other half cycle, with the electron gun on, the ions are formed in an essentially field-free region. Electron energies were able to be measured with a digital voltmeter.

The present ion source was designed to minimize wall

collisions and thus assist in the detection of free radical species present in the reaction system. The gas travelled through the sampling leak and into the ionization chamber by a direct line-of-sight arrangement. Gas samples entered and left the ionizing region through 95% transparent tungsten mesh and then flowed directly into a cold trap and mercury diffusion pump. The background pressure in the mass spectrometer was usually 5×10^{-7} torr, and during operation pressures were normally less than 5×10^{-5} torr. Pressures were measured on a Veeco ionization gauge.

It was found that neither tungsten nor rhenium filaments were suited for use with chlorine monoxide. The emission was very difficult to stabilize and the filament lifetime was rather unsatisfactorily short (often only a few hours). For this reason thoriated iridium filaments were used⁹⁵. These filaments gave steady emission characteristics, and would last through up to several hundred hours of operation, even in the presence of relatively large amounts of chlorine oxides and nitrogen oxides. The lifetime was shortened if the filament was operated at too high a temperature however. Filaments were prepared by coating 0.005 inch diameter iridium wire with finely powdered thoria. The coating was carried out using a cataphoretic process in an alcohol bath⁹⁷.

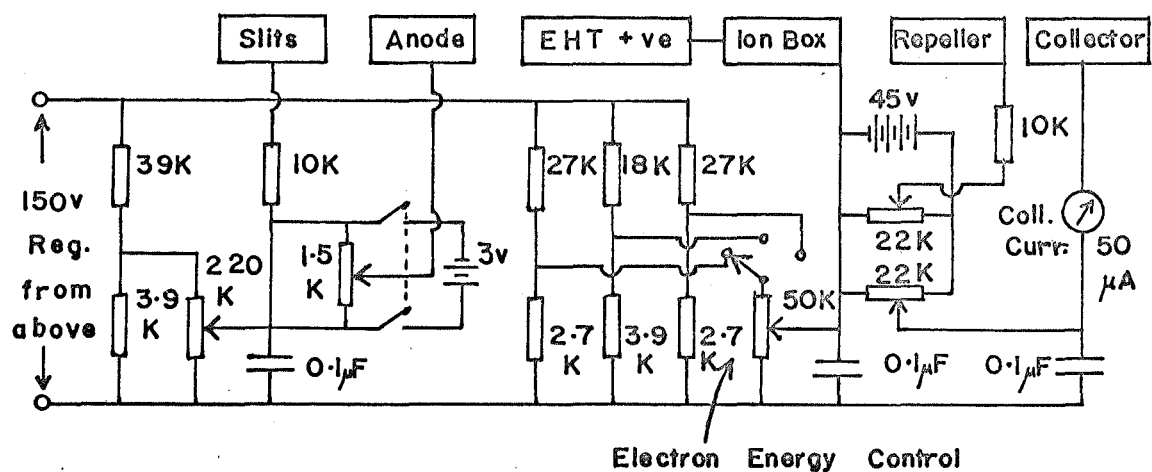
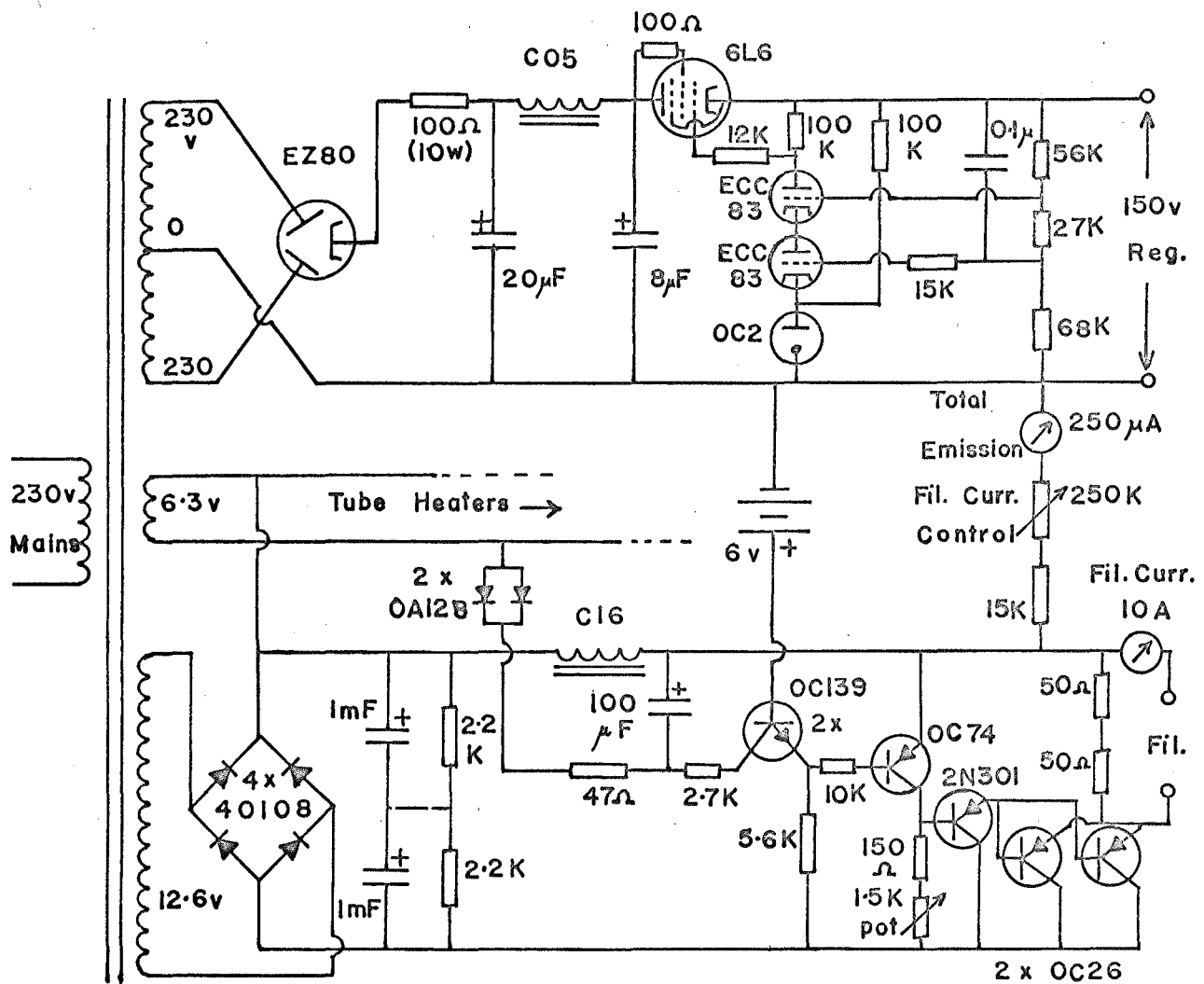
Ion currents were detected by means of a Cary 31 vibrating-reed electrometer. The input to the electrometer

appeared across a load resistor of either 10^9 , 10^{10} , 10^{11} or $10^{12} \Omega$, and the output was coupled to a Leeds and Northrup, high-speed, 10 mV chart recorder with 0.25 second response for full-scale deflection. With this arrangement the limit of ion current detection was about 2×10^{-17} amperes. The sensitivity limit of the mass spectrometer towards Cl_2O and NO_2 , corresponded to partial pressures for these gases of about 2×10^{-5} torr in the reaction system. The limit for NO , N_2 , O_2 , H_2 and argon corresponded to pressures an order of magnitude lower than this figure.

The power supplies for the electromagnet, magnet scanning control, and ion accelerating high voltage were taken from the published circuits of McKinney and co-workers⁹⁸ with minor modifications. The circuit for the filament power supply, emission control, and supply of voltages to various parts of the ion source is shown in Figure 4. It was found necessary to modify the transistorized filament power supply several times, especially when the filament material was changed. The circuit shown is that which was found to be satisfactory for use with thoriated, 0.005 inch diameter iridium wire as the filament material. These power supply units generally proved reliable but certain faults developed on occasions. The most common source of trouble was due to ageing of vacuum tubes; the 6L6 power regulator tubes in the magnet supply proved to be the most frequent offenders in this respect. On several occasions breakdowns occurred in

FIGURE 4

Power Supply for Filament and Emission Control



the insulation of various parts of the high-voltage power supply, particularly in damp or humid weather.

Figure 5 shows schematically the layout of the various parts of the mass spectrometer. Figure 6 shows the actual flow system and mass spectrometer used. Figure 7 shows the mass spectrometer control panel.

2.3 MATERIALS

Matheson "ultra-high purity" oxygen, Matheson "pre-purified" nitrogen (O_2 less than 8 p.p.m.), and welding-grade 99.99% pure argon ($O_2 < 10$ p.p.m.) were used directly from cylinders, the only further purification being drying of gases by passage through cold traps at liquid air (N_2) or dry-ice (O_2 and Ar) temperatures. Industrial grade hydrogen was purified by passage over copper heated to $400^\circ C$ and through a liquid air cooled trap.

Oxygen atoms were generated by discharging argon-oxygen mixtures of between 3 and 20% oxygen content, for hydrogen atoms about 1 to 2% of hydrogen in argon was used, and nitrogen atoms were formed from pure nitrogen with no argon present.

Matheson 98.5% pure nitric oxide was used to obtain nitrogen oxides for titration of atoms. Nitrogen dioxide was obtained by reacting nitric oxide with an excess of purified oxygen. Both NO and NO_2 were purified by trap to trap distillation after the manner described by Nightingale et al⁹⁹.

FIGURE 5

Block Diagram of Mass Spectrometer

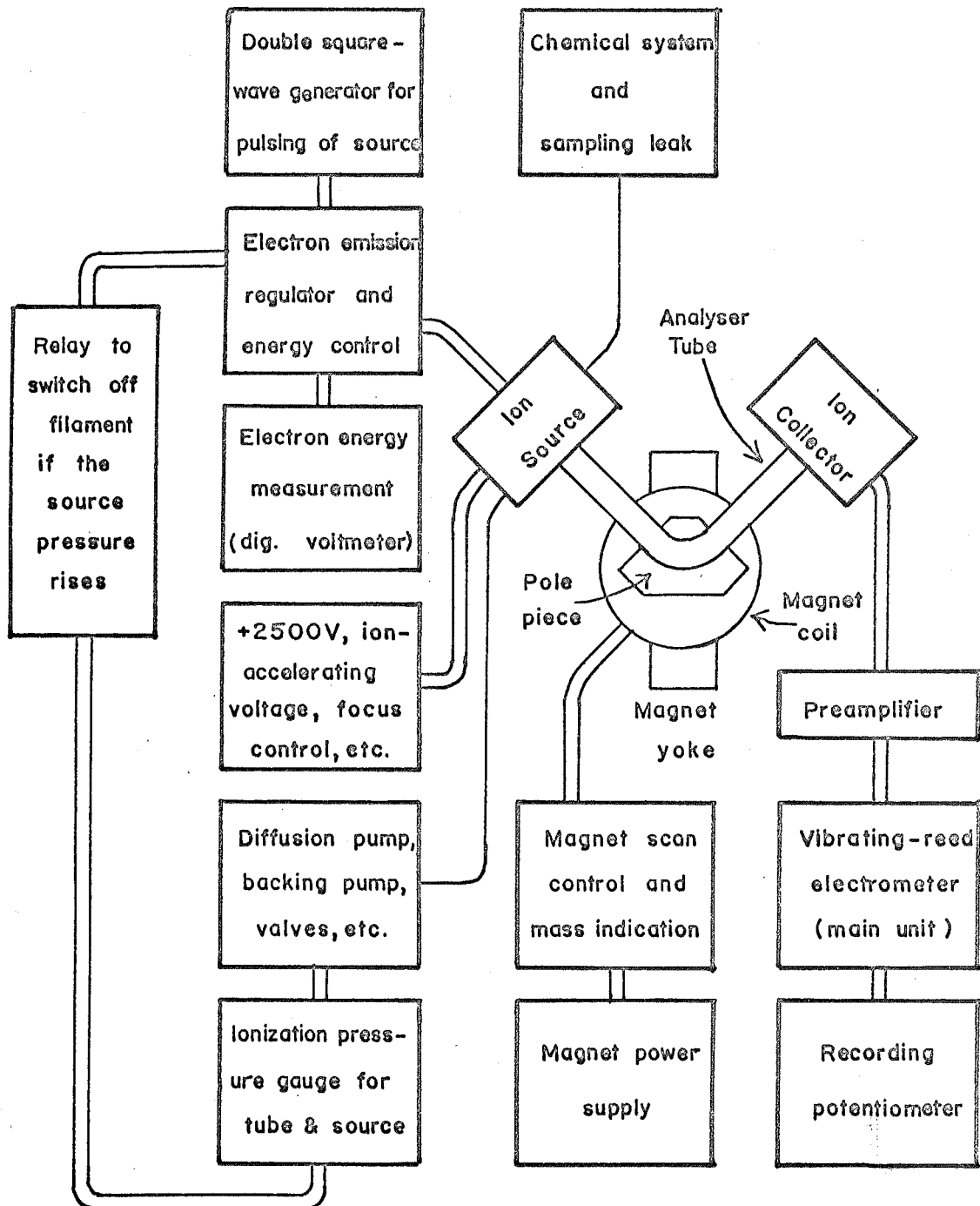


FIGURE 6

Mass Spectrometer and Flow System

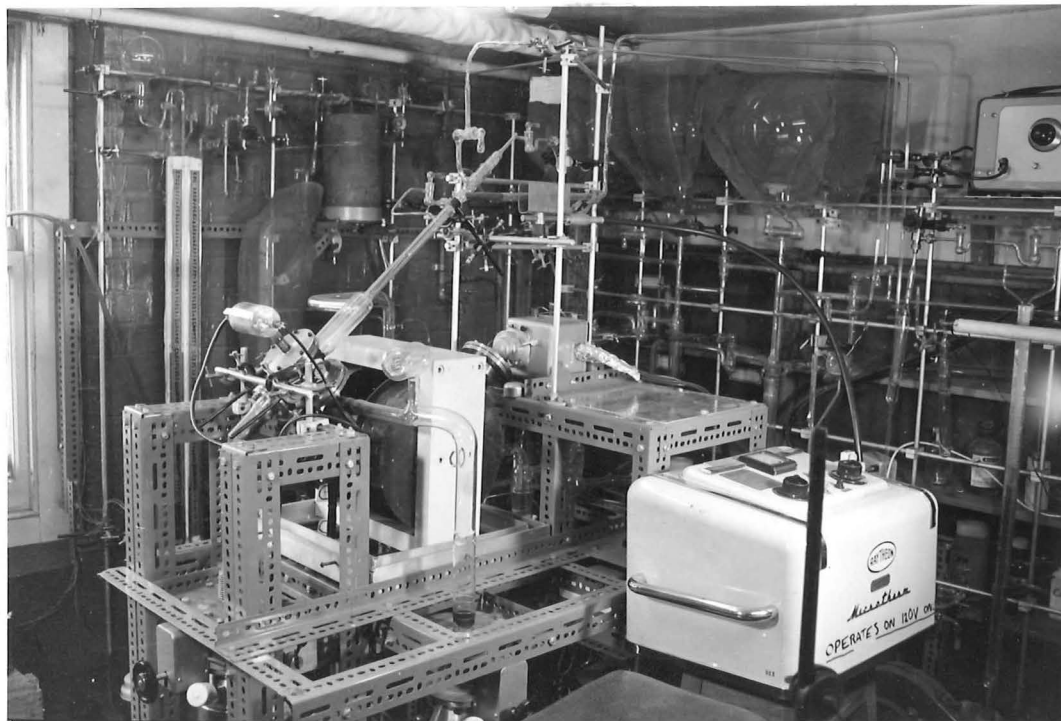
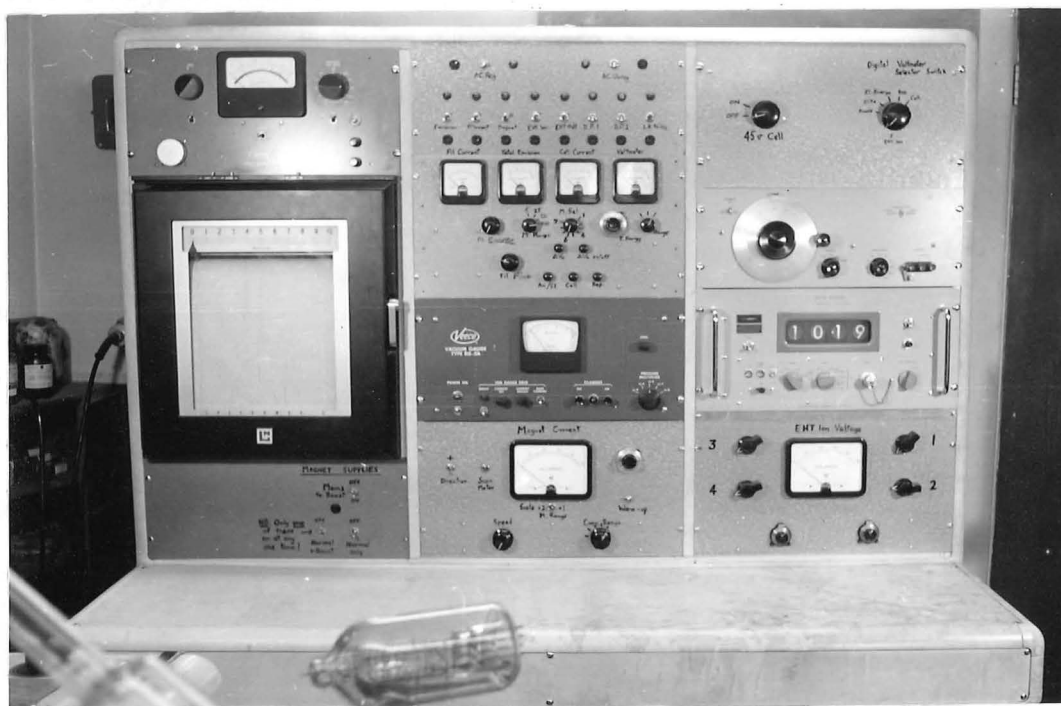


FIGURE 7

Mass Spectrometer Control Panel



Chlorine monoxide was prepared by passage of redistilled chlorine over yellow mercury (II) oxide, the method being patterned after that of Gady¹⁰⁰. A 50 cm reaction column of 35 mm o.d. pyrex tubing was filled with a 1:1 mixture of glass chips and mercury oxide. The top and bottom of the tube were packed with glass wool. The chlorine to be reacted was liquefied in a trap, at liquid air temperature, and the preparative line filled with dried nitrogen to atmospheric pressure. The liquid air was then removed from the chlorine trap and the liquefied gas was allowed to evaporate from the unthermostated trap. As the chlorine evaporated it was carried through the reaction column by a stream of nitrogen at the rate of 50 cc per minute. This technique gave adequate control of the chlorine flow rate and prevented heating in the reaction column. Products were trapped out at liquid air temperature and subsequently purified using a Le Roy still¹⁰¹. The still was shielded by a length of 6 inch diameter cast iron tubing as a precaution against explosion. No explosions were experienced in this work. A sulphuric acid manometer was used to monitor the pressure during distillation, and when the vapour pressure corresponded to that of Cl_2O ¹⁰² the fraction was collected and stored in a blackened bulb. (It may be noted here that the whole of the Cl_2O handling system, and the leads to the reaction system, were blackened to prevent photochemical decomposition.) After purification the product

was analysed for chlorine monoxide content using the iodometric titration method of Spinks¹⁰³. With careful distillation the chlorine monoxide could be obtained with purity greater than 99%, the main impurity being Cl_2 , with possibly traces of H_2O and HOCl . When stored in a blackened bulb such a sample was still 96% pure after two or three months.

All stopcocks in the chlorine oxide preparative and handling systems were lubricated with Kel-F no.90 fluoro-carbon grease. Edwards silicone grease was used on all other joints in the gas handling and reaction systems.

2.4 CALIBRATIONS

Capillary flowmeters were used to record the molecular flow rates of argon or nitrogen and these were calibrated in the following manner. A burette was placed in series with the flowing gas and a soap film was conveyed through the burette by the gas, which had previously been saturated with water vapour. The gas was then dried in a cold trap and passed into the flowmeter. The time required for the soap film to traverse a given volume in the burette was recorded for various values of the registered pressure difference of the mercury manometer, which was incorporated in the flowmeter. The temperature of the gas in the burette was recorded, a correction applied for the presence of water vapour, and the measured flow rates then corrected to 760 torr and 25°C.

A calibration graph was thus constructed for the flowmeter and used in all subsequent experiments. The pressure of the gas entering the flowmeter was at all times regulated to atmospheric by means of a small trap containing butyl phthalate. The outlet tap of the gas cylinder was adjusted so that some of the gas always bubbled out through this trap.

In order to determine partial pressures for different species present in the flow tube during reaction, it was necessary to know the mass spectrometric sensitivities for all gases. Sensitivities for argon, nitrogen, hydrogen and oxygen were measured directly by closing the tap on the pump lead of the flow system, and admitting the gas to the static system. The gas pressure, as indicated on the micro-manometer, and the corresponding mass spectrometric peak height were recorded simultaneously. Over the pressure range 0 to 0.5 torr in the reaction system the peak height was usually found to increase linearly with pressure, to within 2 or 3%, for all of these gases. It was not desirable however to admit NO_2 , NO or Cl_2O to the micromanometer, because of the possibility of damaging the very thin stainless steel diaphragm inside that instrument. Sensitivities for these gases were therefore determined indirectly, by preparing mixtures with argon of known composition. The mixtures were introduced to the mass spectrometer, and the sensitivities of the gases, relative to argon, determined from the ratio of parent peak heights in the spectrum. It was found that

relative sensitivity values once determined remained constant to within about 5% over periods of time, provided constant ion source conditions prevailed. If small variations were observed in relative sensitivity factors they were assumed to be the result of linear changes, and were time-interpolated.

Mixtures of chlorine monoxide and argon were prepared using a sulphuric acid manometer. For mixtures of NO and NO₂ with argon a Texas Instruments, Model 144, 0-300 torr, quartz spiral gauge was used. In the case of NO₂, allowance was made for the fact that when the NO₂ pressure was measured during preparation of the mixture, an appreciable proportion was present as N₂O₄¹⁰⁴. Under the conditions in the flow system when relative sensitivities were determined, the equilibrium proportion of N₂O₄ was negligible. It may be shown that the dissociation of N₂O₄ to NO₂ is rapid enough for complete dissociation before mass spectrometric sampling, even in the fastest flow conditions attainable¹⁰⁵.

Typical values for the sensitivities of gases used, all referring to the heights of parent peaks relative to argon at mass 40, were Cl₂O 0.045, NO₂ 0.055, NO 0.51, N₂ 0.53, O₂ 0.38, and H₂ 0.14.

2.5 EXPERIMENTAL PROCEDURE

(i) Mass Spectrometric Sensitivities

Prior to each experiment, where mass spectrometer readings were required, it was necessary to allow the various power supplies sufficient warm-up time, in order to obtain stable output signals. From time to time it was also necessary to "tune" the overall sensitivity of the instrument to an optimum level. Once the filament current had been adjusted to a suitable value, the factor having the most marked influence on the sensitivity was the position of two small external magnets. The purpose of these magnets was to provide a weak magnetic field inside the ion source, and to align the ionizing electron beam. To optimize the sensitivity these small magnets were moved until a suitable orientation was found. The magnets were then clamped in place and left undisturbed as long as possible.

In order to save time at the commencement of an experimental run, only the sensitivity of the bulk carrier gas to be used was directly measured. The carrier gas was always argon or nitrogen. Sensitivities of oxygen and hydrogen were determined in preliminary experiments, and expressed relative to that of argon, as measured in the same preliminary experiment. When successive determinations of the carrier gas sensitivity were constant to within 1 or 2% over a ten minute period, the flows of gases were adjusted to the values desired and the carrier gas peak height

immediately recorded. This peak height together with the previous steady sensitivity value, gave the pressure of the carrier gas present in the flowing reaction gas mixture, in the zone near the mass spectrometer sampling leak. With fast flow conditions there was an appreciable pressure drop between the micromanometer inlet and the sampling leak, and it was not possible therefore to measure the carrier gas pressure directly. Essentially the same procedure was carried out in reverse at the end of an experimental run. The carrier gas peak was recorded immediately prior to turning off gas flows, and then sensitivity measurements taken straight away on the carrier gas, with the pump lead closed as before. Initial and final carrier gas pressure values, determined in this way, normally agreed to within 2 or 3%, which was the estimated error in each value. If the two pressure values did not agree to within 5% the experiment was disregarded.

The pressures of all other gases present in the reaction zone during an experiment were determined from the measured parent peak height, the known carrier gas sensitivity, and the sensitivity of the gas in question relative to that of the carrier. Relative sensitivities were determined directly or indirectly by the methods described previously.

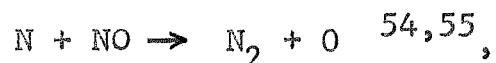
There was always a certain amount of fluctuation in the overall sensitivity of the mass spectrometer towards all gases, during the course of an experiment. Experiments

normally lasted between three and six hours. The peak height of the carrier gas was therefore monitored at frequent intervals during an experiment, and provided a convenient means of following sensitivity fluctuations. Since the pressure of this gas remained constant, changes in the peak height reflected changes in sensitivity alone. Sensitivities were usually found to drift linearly with time and therefore they were time-interpolated, and a variable correction applied to intermediate readings.

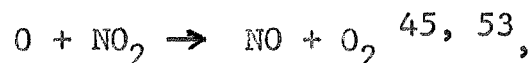
(ii) Titration of Atom Concentrations

The following reactions were used for titrating atom concentrations:

(i) Nitrogen atoms were determined using

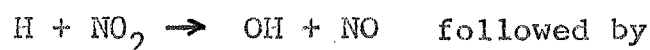


(ii) Oxygen atoms were estimated using NO_2 , the reaction being



(iii) Hydrogen atoms were also titrated with NO_2 .

In this case the reaction sequence is⁵⁸



In cases (i) and (ii) the stoichiometry is 1:1, atoms:titrant. For hydrogen atoms however, two atoms react

with three molecules of NO_2 . The stoichiometry of these titrations has been confirmed by electron spin resonance^{40,41}, and more recently by Elias¹⁰⁶ who measured the decrease in pressure when volumes of partially dissociated gases were suddenly isolated.

The procedure followed in the present study was to add an excess of titrant gas to the flow system, and to observe the decrease in titrant parent peak when the microwave discharge was activated, and atoms produced. Generally about a 2-fold or 3-fold excess of titrant gas was used. From the observed peak decrease and known titrant gas sensitivity, the atom concentration was calculated. The titration gas inlet jet was sufficiently far from the sampling leak for the titration reactions to be complete before analysis. The decrease in atom concentration along the tube, between jet and leak, was negligible in the present poisoned system with the fast flow rates used.

Normally, atom concentrations were titrated at the beginning and at the end of each experiment, although on occasions checks were made more frequently than this. It was found that for a given microwave power level, atom concentrations were usually reproducible to within $\pm 5\%$ over several hours, regardless of how many times the discharge was activated and extinguished.

(iii) Primary Rate Constant Measurements

Measurements of the primary rate constants for the reactions of atoms with chlorine monoxide were made using the largest possible excesses of atoms, relative to Cl_2O . Typically the atom excess was 10-fold, but was always greater than 3-fold. There were several benefits from using this approach. Firstly, the importance of secondary reactions was minimized, virtually all of the Cl_2O being consumed by the primary reaction with atoms. Secondly, the rate constant values obtained were not critically dependent on the mass spectrometric sensitivity of Cl_2O , since the partial pressure of Cl_2O decayed almost exponentially with time in a large excess of atoms. Furthermore, under these conditions it was not essential to use highly pure Cl_2O , since the reactions of each of the atoms with likely impurities were all slower than the corresponding reactions with Cl_2O . Nevertheless in all experiments the Cl_2O used was more than 90% pure.

There were two factors which imposed limitations on the use of very high excesses of atoms. Firstly, if the atom concentration was too high the lifetime of even minute amounts of Cl_2O was very short. Serious errors were thus introduced in the measurement of the very short reaction times. In addition, the rate is then highly dependent on the efficiency of mixing of the reactants. Atom concentrations were normally adjusted so that the "half-life" of Cl_2O

corresponded to about 0.5 to 2 cm distance in the reaction flow tube. Once the atom pressure had been set at a suitable value, the second limitation governing the size of the atom excess was met, namely, the sensitivity limit of the mass spectrometer towards Cl_2O .

In virtually all experiments where primary rate constants were determined, readings were taken with the Cl_2O jet less than 3 cm. from the mass spectrometer sampling leak, i.e. within about 3 msec. reaction time. It may be shown, using the expression quoted in section 1.3(iii), that the viscous pressure drop in this region is not more than 3% of the total pressure, with the flow conditions normally prevalent. Taking even the most unfavourable case and applying corrections to the calculation of the rate constant, k , it may be shown that the pressure drop correction to k is always less than 1%. This is because correction terms in the same direction appear on top and bottom lines of the expression used in calculating k when the Cl_2O decay is nearly exponential. Pressure drop corrections were ignored in these measurements since the total estimated error from other sources was typically 15 to 20%.

The procedure followed in measuring rate constant values was as follows. The mass spectrometer sensitivity was checked, the mixing jet position set, and the gas flows adjusted. The mass spectrometer was focussed on to mass 86 (parent Cl_2O^+) and the background signal level measured with Cl_2O absent. Chlorine monoxide was then admitted and the

peak height measured with and without the discharge on, at least three or four times. Finally the background signal was checked again. Averages were then taken if the signals were consistent and stable.

It should be noted that "blanks" were performed in these experiments, and indeed in all others, including titrations. For example, in these measurements Cl_2O (or titrant gas) was admitted to a stream of argon, with no diatomic gas present, and the discharge activated. It was thus confirmed that no Cl_2O (or titrant) was consumed by argon metastables, trace impurities in the argon, or by photolysis from the discharge region.

(iv) Measurements of Reaction Stoichiometry

The procedure followed here was similar to that described above, except that in these experiments the longest possible reaction times were used, and an excess of Cl_2O , relative to atoms, was present. Long reaction times were obtained by moving the Cl_2O jet as far as possible from the mass spectrometer sampling leak, and also by operating the flow system with the Roots pump switched off. Reaction stoichiometry determinations were carried out by alternately measuring the consumptions, by the atoms, of atom titrant gas and excess Cl_2O , at long reaction times. In these experiments the purest possible samples of chlorine monoxide (> 99%) were used in order to avoid complicating effects from reactions

of impurities.

In these measurements, where the full length of the flow tube was used, the pressure drop down the tube will be considerably larger than in rate constant measurements. In fact the drop was up to 10% of the total pressure, with the conditions used. However, since the Cl_2O jet at its "long time" position was at almost exactly the same position as the titrant gas inlet jet, the effect of pressure drop can be ignored. The stoichiometry is expressed as the ratio between Cl_2O and titrant consumed and both of these measurements are affected equally by the pressure drop.

(v) Product Analyses

Checks were carried out on all reaction systems for the various products and intermediates present. Generally these measurements were only made on a semi-quantitative basis, as it was not possible to determine absolute mass spectral sensitivities for many of the products, or for any of the free radical intermediates. For example, H_2O and HCl both possessed large and persistent background peaks which were usually much larger than the increases in these peaks due to reaction products. Observations of this type were made at both short and long reaction times and care was taken to perform "blanks" in all cases.

(vi) Temperature

Temperatures were measured on a mercury thermometer placed adjacent to the reaction tube. All experiments were performed at room temperature, which was always between 21 and 25°C.

2.6 CALCULATION OF RESULTS(i) Flow Velocities in Tube

Flow velocities in the reaction tube were calculated according to the expression,

$$\text{Linear Flow Velocity} = \left(\frac{dV}{dt}\right) \cdot \frac{T \cdot K}{P}$$

where $\frac{dV}{dt}$ = flow of principal inert carrier gas (Ar or N₂) in cm³.sec⁻¹ at 1 atm. and 25°C as indicated by the capillary flowmeter,

T = temperature in degrees Kelvin,

P = pressure of carrier gas in flow tube in torr,

and K is a constant which is a function of the tube radius, and the temperature and pressure at which the flowmeter was calibrated.

For the tube used in these experiments the radius was 0.85 cm, and the flowmeter was calibrated at 1 atm. and 25°C. The corresponding value of K = 1.123 and the flow velocity is then given directly in cm.sec⁻¹.

Note that it was necessary only to monitor the flow rate of one gas with a flowmeter, and provided the pressure of this gas in the tube was known, the flow velocity was fixed.

(ii) Reaction Times

Reaction time is given simply by the expression

$$\text{Time} = \frac{\text{Jet distance}}{\text{Flow velocity}} .$$

(iii) Partial Pressures

The partial pressure of any gas Q in the flow tube was calculated by the expression

$$P(Q) = \frac{Q}{S(Q)}$$

where $P(Q)$ = partial pressure of Q,

Q = peak height of Q parent peak in mass spectrum,
and $S(Q)$ = absolute sensitivity of the mass spectrometer
towards gas Q.

Note that for most gases $S(Q)$ was measured indirectly and interpolated during the experiment to the time of measurement of peak Q, as has been described previously.

(iv) Rate Constants

Bimolecular rate constants were calculated according to the integrated expression

$$k = \frac{\log_e \left[\frac{a(b-x)}{(a-x)b} \right]}{(b-a) t} \quad \text{--(a)}$$

where a and b = reactant concentrations at time 0,

x = concentration of a and b which have reacted
at time t,

t = time of reaction,

k = second-order rate constant.

In the case where one reactant is in large excess, as was approximately the case when primary rate constants were measured, the expression reduces to,

$$k \approx \frac{\log_e \left[\frac{a}{a-x} \right]}{b \cdot t} \quad \text{--(b)} \quad (\text{for } b \gg a).$$

In computation of results both forms were used. Once it was established that the reaction being measured was in fact the primary atom reaction the full form (a) was used, and all rate constant values presented in later tables have been calculated in this manner. The units adopted for k in this work are those of $\text{cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$.

CHAPTER 3

THE REACTION OF OXYGEN ATOMS WITH CHLORINE MONOXIDE

3.1 THE MASS SPECTRUM OF CHLORINE MONOXIDE

The mass spectrum of chlorine monoxide does not appear to have been reported previously. Table 1 records the spectrum as observed in the present study.

Spectra were observed using an ionizing electron energy of 50 volts and gas pressures in the ion source of about 1×10^{-5} torr. Cl_2O was admitted to the static reaction system at a pressure of around 0.1 torr and the system allowed to condition for at least 15 minutes before a reproducible spectrum was obtained. Prior to this the Cl_2O^+ peaks were somewhat smaller, and the HCl^+ peaks a little larger, than those finally obtained in the reproducible mass spectrum. This was due to some interaction of the Cl_2O with the handling system or the ion source; most probably the phosphoric acid wall coating. The same conditioning procedure was usually carried out before recording Cl_2O peaks in kinetic and other experiments.

Examination of Table 1 indicates that the ions containing one or more chlorine atoms are all present in the expected isotopic intensity ratios. It is also apparent that a considerable proportion of the Cl_2O molecules are fragmented in the ionization process, the peaks corresponding to ClO^+ and Cl^+ being the largest present in the spectrum.

Table 1
Mass Spectrum of Cl₂O

<u>Mass No.</u> <u>a.m.u.</u>	<u>Origin of Peak</u>	<u>Relative Height of Peak*</u>
16	O ⁺	2.8
17	OH ⁺	1.3
18	H ₂ O ⁺	3.4
28	N ₂ ⁺ , CO ⁺	6.0
35	³⁵ Cl ⁺	58.3
36	H ³⁵ Cl ⁺	23.1
37	³⁷ Cl ⁺	18.7
38	H ³⁷ Cl ⁺	7.4
44	CO ₂ ⁺	7.2
51	³⁵ ClO ⁺	100.0
52	H ³⁵ ClO ⁺	9.2
53	³⁷ ClO ⁺	32.0
54	H ³⁷ ClO ⁺	2.9
70	³⁵ Cl ³⁵ Cl ⁺	15.9
72	³⁵ Cl ³⁷ Cl ⁺	10.2
74	³⁷ Cl ³⁷ Cl ⁺	1.6
86	³⁵ - ³⁵ Cl ₂ O ⁺	41.5
88	³⁵ - ³⁷ Cl ₂ O ⁺	26.5
90	³⁷ - ³⁷ Cl ₂ O ⁺	4.2

(Other peaks all < 1% of mass 51)

*Relative peak heights expressed as % of most abundant peak (i.e. Mass 51). Contributions to the above peaks from background mass spectrum have been subtracted.

Ion Source gas pressure 1×10^{-5} mm.

Electron Energy 50 volts.

This is not surprising in view of the relatively weak Cl-O bond in the Cl_2O molecule ($D^0_{298} = 35 \text{ kcal.mole}^{-1}$)⁸¹, and the relatively high electron energy used in obtaining the spectrum. In spite of this, the parent Cl_2O^+ peaks are still sufficiently intense for partial pressures of Cl_2O to be conveniently monitored. All such readings were taken on the most intense of the Cl_2O^+ peaks (Mass 86) in order to obtain optimum sensitivity.

The persistence of peaks due to HCl , HOCl and H_2O in mass spectra of even the most highly purified Cl_2O samples, indicates that these species probably arise from reaction with the phosphoric acid wall coating or tap grease in the system. The Cl_2^+ peaks may originate from the same source but could also arise from secondary reaction inside the ion chamber, or at chlorine-contaminated surfaces in the ion chamber. Samples of Cl_2O in which the Cl_2 content was much less than 1% produced Cl_2^+ peaks of about one-third of the intensity of the Cl_2O^+ peaks. This meant that mass spectrometric analysis of Cl_2O , during separation from Cl_2 in the LeRoy still, was not a reliable indication of its purity. For this reason the titration method, previously referred to, was used.

Peaks of CO_2^+ and CO^+ probably arise from interaction of Cl_2O with carbon impurities in the ion source filament.

3.2 REACTION PRODUCTS

Products were observed under reaction conditions where the initial O atom and Cl₂O partial pressures were nearly equal, both being approximately 2×10^{-3} torr. Argon and molecular oxygen pressures were 0.3 torr and 8×10^{-3} torr respectively, and the reaction time was 100 msec. When the discharge was activated large increases were found at mass 70 (Cl₂⁺) and mass 32 (O₂⁺), corresponding to the formation of the stable products Cl₂ and O₂. No increases were observed at mass 36 (HCl⁺) or at any other mass numbers.

When Cl₂O was admitted, in the absence of O atoms, a small increase was observed at mass 70. This is to be expected from the mass spectrum of Cl₂O (see Table 1). When the microwave discharge was activated the increase at mass 70 was over 15 times as large as that observed in the absence of atoms. This leaves no doubt that Cl₂ is a product of the reaction.

When the discharge was turned on, in the absence of Cl₂O, the mass 32 (O₂⁺) peak decreased as a natural consequence of the dissociation of some of the molecular oxygen to atoms. When Cl₂O was admitted to the flow system, there was an overall increase at mass 32 when the oxygen was discharged. The magnitude of the net increase at mass 32, when the discharge was on and Cl₂O was admitted, was only about 70% of that expected for complete conversion of O + Cl₂O to O₂ and Cl₂. At the same time, well over 95% of the Cl₂O had been removed by reaction. This discrepancy in O₂ is attributed to the

presence of relatively long-lived ClO radicals.

The presence of ClO, even after 100 msec, was shown directly by the observation that the decrease in peak height at mass 51 (ClO^+), when the discharge was turned on, was very much less, proportionately, than the simultaneous decrease at mass 86 (Cl_2O^+). With the reaction conditions quoted above, the mass 86 peak fell to less than 5% of its initial value, while at the same time the mass 51 peak was reduced to about 33% of its former value. ClO radicals were similarly detected at short reaction times when Cl_2O was in excess, at equal reactant concentrations, and in a slight excess of O atoms. With a larger excess of O atoms (> 3 -fold) ClO radicals were not detectable even at 0.5 msec reaction time. It is not possible to estimate the absolute concentration of ClO radicals since the mass spectrometric sensitivity of ClO is unknown, and furthermore the contribution to mass 51 peak from Cl_2O is relatively large.

3.3 STOICHIOMETRY OF THE REACTION

Measurements of the overall reaction stoichiometry are shown in Table 2. The relative excess of Cl_2O present ($= (\text{Cl}_2\text{O})_{\text{total}} : (\text{Cl}_2\text{O})_{\text{consumed}}$) ranged from 1.86:1 to 5.51:1 at O atom pressures between 1.0×10^{-3} and 2.2×10^{-3} torr. It appears that there is a slight dependence of the stoichiometry on the total pressure. The mean ratio of Cl_2O to O consumed was 0.72 ± 0.15 at 0.24 torr, and 0.88 ± 0.15 at 0.32

Table 2Stoichiometry of the $O+Cl_2O$ ReactionReagent partial pressures in microns (10^{-3} torr)(1) (Argon) = 305; (O_2) = 9.2; Time 100 msec.

$(O)_o$	$(Cl_2O)_o$	$\Delta(Cl_2O)$	$\frac{\Delta(Cl_2O)}{(O)_o}$	Relative excess of Cl_2O present*
0.99	3.00	0.80	$0.81 \pm 0.15^+$	3.75
0.96	4.58	0.96	1.00 ± 0.25	4.77
1.04	4.35	0.89	0.86 ± 0.25	4.89
0.96	4.37	0.79	0.82 ± 0.10	5.51
Mean = 0.88 ± 0.15			(Total pressure = 0.32 torr)	

(2) (Argon) = 236; (O_2) = 8.6; Time 100 msec.

$(O)_o$	$(Cl_2O)_o$	$\Delta(Cl_2O)$	$\frac{\Delta(Cl_2O)}{(O)_o}$	Relative excess of Cl_2O
2.11	2.60	1.40	0.67 ± 0.15	1.86
2.20	5.28	1.67	0.76 ± 0.10	3.17
1.96	4.94	1.50	0.77 ± 0.20	3.28
2.03	4.54	1.38	0.68 ± 0.10	3.29
Mean = 0.72 ± 0.15			(Total pressure = 0.24 torr)	

*Relative excess of $Cl_2O = \frac{(Cl_2O)_o}{\Delta(Cl_2O)}$

+Total estimated error in $\frac{\Delta(Cl_2O)}{(O)_o}$

torr. There is no obvious dependence on the size of the Cl_2O excess at constant total pressure.

3.4 THE RATE CONSTANT FOR THE PRIMARY REACTION

The rate constant for the primary reaction of O atoms with Cl_2O was measured using an excess of atomic oxygen. The results are given in Table 3. The mean value found for the primary rate constant k_1 is $8.3 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$, with a standard deviation of $1.4 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$. The total estimated error in the measurements of k_1 is about equal to the standard deviation. The observed values of k_1 show no obvious dependence on the size of the excess of O atoms, on the reaction time, or on the total pressure.

3.5 DISCUSSION

The observations described in sections 3.2, 3.3 and 3.4 can be explained satisfactorily by the following series of reactions:



where $k_1 = 8.3 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (this work),



where $k_2 > 6 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 87),



where $k_3 > 4 \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 22),



Table 3

Measurement of the Rate of the Primary Reaction

Reagent partial pressures given in microns (10^{-3} torr).

(Argon)	(O ₂)	(O) _o	(Cl ₂ O) _o	(Cl ₂ O) _t	t msec	k ₁ cm ³ .mole ⁻¹ . sec ⁻¹
144	18.3	1.52	0.138	0.077	1.08	6.8 x 10 ¹²
"	"	"	0.148	0.053	1.90	6.9 "
"	"	"	0.159	0.090	0.857	8.3 "
"	"	"	0.155	0.059	1.67	7.3 "
"	"	"	0.168	0.038	2.89	6.6 "
"	"	"	0.145	0.083	0.993	7.1 "
140	7.8	1.47	0.148	0.080	1.01	7.9 x 10 ¹²
"	"	"	0.149	0.107	0.597	7.2 "
"	"	"	0.141	0.025	3.03	7.6 "
"	"	1.12	0.156	0.066	1.84	8.2 "
"	"	"	0.150	0.098	0.872	8.4 "
"	"	"	0.158	0.078	1.47	8.3 "
141	9.2	1.13	0.158	0.068	1.46	10.0 "
"	"	"	0.156	0.090	0.956	9.6 "
"	"	"	0.139	0.036	2.32	10.1 "
"	"	"	0.160	0.110	0.615	10.3 "
"	"	"	0.089	0.045	1.21	9.5 "
137	31.8	2.19	0.184	0.063	1.17	8.0 "
"	"	"	0.161	0.088	0.531	9.7 "
"	"	"	0.210	0.098	0.840	7.8 "

(Table 3 contd)

(Argon)	(O ₂)	(O) _o	(Cl ₂ O) _o	(Cl ₂ O) _t	t msec	k ₁ cm ³ .mole ⁻¹ . sec ⁻¹	
137	31.8	2.19	0.206	0.056	1.55	7.4 x 10 ¹²	
"	"	"	0.213	0.110	0.663	8.6	"
144	8.3	0.99	0.110	0.065	1.04	9.8	"
"	"	"	0.102	0.044	1.97	8.4	"
"	"	"	0.147	0.042	2.79	9.0	"
"	"	0.72	0.146	0.106	0.798	10.6	"
"	"	"	0.129	0.069	1.68	10.0	"
"	"	"	0.119	0.045	2.62	10.1	"
151	5.4	0.598	0.101	0.067	1.22	10.7	"
"	"	0.546	0.097	0.051	2.27	10.1	"
"	"	0.503	0.121	0.056	3.04	10.2	"
"	"	0.477	0.101	0.070	1.86	8.0	"
150	7.1	0.94	0.172	0.089	1.85	7.5	"
"	"	"	0.144	0.096	0.948	8.6	"
"	"	"	0.142	0.047	2.84	8.1	"
"	"	"	0.145	0.090	1.44	6.8	"
"	"	"	0.128	0.054	2.44	7.4	"
139	29.5	1.83	0.155	0.094	0.836	6.2	"
"	"	"	0.166	0.074	1.55	5.5	"
"	"	"	0.184	0.057	2.26	5.5	"
"	"	"	0.188	0.092	1.28	5.8	"

Mean k₁ = (8.3 ± 1.4) x 10¹² cm³.mole⁻¹.sec⁻¹.

which is likely to be slow in the present system with walls poisoned with phosphoric acid. Ogryzlo⁹³ found a value of $k_4 = 0.8 \text{ sec}^{-1}$ in a similarly poisoned system at 10°C .



where $k_5 = 1.7 \times 10^{10} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 87).

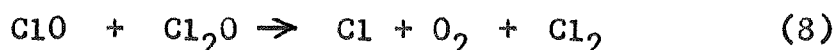
The following reactions are too slow to be considered in the present system:



This reaction is $6.4 \text{ kcal} \cdot \text{mole}^{-1}$ endothermic⁸¹, and furthermore the reverse reaction⁸⁸ has an activation energy of $3.1 \text{ kcal} \cdot \text{mole}^{-1}$. This means that reaction (6) has an activation energy of $9.5 \text{ kcal} \cdot \text{mole}^{-1}$ and is therefore very slow at room temperature (k_6 must be less than $10^7 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$).



where $k_7 = 10^8 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 22).



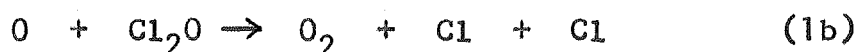
where $k_8 = 5.3 \times 10^7 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 22).



where $k_9 \simeq 10^{17} \text{ cm}^6 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ (reference 37).

It may be shown that at the pressures used in the present experiments this termolecular process will be at least 100 times slower than reaction (3).

In addition, the alternative primary steps



have been assumed to be negligibly slow in comparison with reaction (1). Reaction (1a) although exothermic by 78 kcal.^{mole⁻¹} is a 4-centre reaction²² and it requires considerable molecular rearrangement. It is almost certain therefore that (1a) is at least several orders of magnitude slower than reaction (1). Reaction (1b) may be ruled out as unlikely in that it requires the simultaneous breaking of two Cl-O bonds in the transition complex, otherwise it becomes step (1d). Furthermore, reaction (1b) will tend to produce stoichiometry greater than 1:1, Cl₂O consumed:O atoms, as it is a chain branching step; this contradicts the present observations. Reactions (1c) and (1d), although both possible thermochemically, have been excluded on the following grounds. No evidence was found for the presence of ClO₂, or its isomer Cl-O-O, until relatively long reaction times, in the flash photolysis of Cl₂O²². The ClO₂ in this case was formed by reaction (7) above. There were no mass peaks detectable at masses 67 or 69(ClO₂⁺) in the products in the present system. Finally, if ClO₂ was formed in the early stages of the reaction, it would undergo the rapid secondary reaction



where $k_{10} > 2.4 \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 87).

k_{10} is some three times greater than the observed k_1 .

If process (1c) were an important primary step, then it would be expected that observed values of k_1 would show a trend towards lower values at long reaction times, and in small excesses of O atoms. This would be due to competition for O atoms between the primary step and the known faster step (10). Cl-O-O would almost certainly undergo a similar rapid reaction with O atoms. No trend towards lower k_1 values was observed. On the basis of this and the other evidence above, steps (1c) and (1d) are ruled out. The values of k_1 in Table 3 are therefore thought to represent the rate of reaction (1) alone.

The sequence of reactions (1)-(5) satisfactorily accounts for the observed formation of Cl_2 and O_2 as products. The relatively slow rate of reaction (5) explains the observed persistence of ClO radicals in the present reaction system. The stoichiometry may be considered as follows.

(i) If reaction (4) is assumed to be very fast, then reaction (3) may be neglected. The overall stoichiometry with only a moderate excess of Cl_2O present would be given by reactions (1) + (2) + (4), i.e. three O atoms would react for each molecule of Cl_2O consumed.

(ii) If reaction (4) is again assumed very fast, and if the excess of Cl_2O becomes very large, reaction (2) may also be neglected. The stoichiometry in this case is determined

by reactions (1) + (5), i.e. 1:1,0 atoms:Cl₂O consumed would be observed.

(iii) If on the other hand reaction (4) is negligibly slow, then with a moderate excess of Cl₂O the reaction sequence (1) + (2) + (3) will produce 1:1 stoichiometry.

(iv) With reaction (4) assumed very slow and a very large Cl₂O excess, the stoichiometry is again given by (1) + (5), i.e. it is again 1:1.

The observation that the stoichiometry is given by $\frac{\Delta \text{Cl}_2\text{O}}{\Delta 0} \approx 0.8$ implies that reactions (2) and (4) are both significant in the present system where the Cl₂O excess is only moderate ($\leq 5.5:1$). That is to say, the actual situation lies somewhere between cases (i) and (iii) above, and there is competition for chlorine atoms by the homogeneous reaction (3) and the wall reaction (4). The observed slight dependence of the stoichiometry on pressure is consistent with this explanation. At lower pressures, wall recombination by reaction (4) becomes relatively more important than at higher pressures. Hence, the stoichiometry, $\frac{\Delta \text{Cl}_2\text{O}}{\Delta 0}$, will move nearer to case (i) above, and is expected to be lower, as is observed.

Finally, the absence of any marked trend in stoichiometry as the excess of Cl₂O over 0 atoms was increased from two-fold to five-fold, suggests that reaction (2) is somewhat faster than reaction (1). It would be expected that as the excess of Cl₂O increases, the stoichiometry would move towards cases

(ii) or (iv) above, i.e. it should show a trend towards 1:1 at larger Cl_2O excesses. This trend is not observed, and this indicates that reaction (2) is still important in determining the overall stoichiometry, even in the presence of a five-fold excess of Cl_2O . This can only be the case if reaction (2) is at least as rapid as reaction (1).

A simple analysis may be applied to reactions (1) to (5) as follows.

$$-\frac{d(\text{Cl}_2\text{O})}{dt} = k_1(0)(\text{Cl}_2\text{O}) + k_3(\text{Cl})(\text{Cl}_2\text{O}) \quad \dots(a)$$

$$-\frac{d(0)}{dt} = k_1(0)(\text{Cl}_2\text{O}) + k_2(0)(\text{ClO}) \quad \dots(b)$$

$$\begin{aligned} \frac{d(\text{Cl})}{dt} &= k_2(0)(\text{ClO}) - k_3(\text{Cl})(\text{Cl}_2\text{O}) - k_4(\text{Cl}) \\ &= 0, \text{ if a stationary state is assumed for} \\ &\quad \text{atomic chlorine.} \end{aligned}$$

Therefore

$$(\text{Cl})_{\text{S.S.}} = \frac{k_2(0)(\text{ClO})}{k_3(\text{Cl}_2\text{O}) + k_4}$$

If expression (a) is divided by expression (b), and $(\text{Cl})_{\text{S.S.}}$ is substituted in the resulting expression, the result is obtained that

$$\begin{aligned} \frac{d(\text{Cl}_2\text{O})}{d(0)} &= 1 - \frac{k_2 k_4(0)(\text{ClO})}{[k_3(\text{Cl}_2\text{O}) + k_4][k_1(0)(\text{Cl}_2\text{O}) + k_2(0)(\text{ClO})]} \\ &= \frac{\Delta(\text{Cl}_2\text{O})}{\Delta(0)} \\ &= \text{Overall stoichiometry at long times.} \end{aligned}$$

Now the observed value of $\frac{\Delta(\text{Cl}_2\text{O})}{\Delta(0)}$ is 0.8 (if an average is taken).

$$\text{Therefore } \frac{k_2 k_4 (0)(\text{ClO})}{[k_3(\text{Cl}_2\text{O}) + k_4][k_1(0)(\text{Cl}_2\text{O}) + k_2(0)(\text{ClO})]} \simeq 0.2$$

If Cl_2O is in a 5:1 excess, then most of the O atoms will be consumed by reaction (1), so that as an approximation reaction (2) may be neglected. The equation then reduces to

$$\frac{k_2 k_4 (\text{ClO})}{[k_3(\text{Cl}_2\text{O}) + k_4] k_1 (\text{Cl}_2\text{O})} \simeq 0.2$$

Now if Cl_2O is in five-fold excess, then (Cl_2O) is almost certainly greater than $5(\text{ClO})$

$$\text{or } \frac{(\text{ClO})}{(\text{Cl}_2\text{O})} < \frac{1}{5}$$

Furthermore with phosphoric acid poisoned walls, k_4 is probably less than $k_3(\text{Cl}_2\text{O})$, and taking even the pessimistic view that reaction (4) is in fact the most important process removing Cl atoms, then

$$\frac{k_4}{k_3(\text{Cl}_2\text{O}) + k_4} \leq 1$$

Therefore, inserting these values in the above expression,

$$\frac{k_2}{k_1} \cdot \frac{1}{1} \cdot \frac{1}{5} \geq 0.2$$

$$\text{or } k_2 \geq k_1$$

The overall result of this treatment is that a conservative lower limit for k_2 is obtained which indicates that $k_2 = k_1$.

More generally it can be expressed as

$$k_2 \geq 8 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}.$$

This is consistent with the lower limit of $6 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ found for k_2 by Clyne and Coxon⁸⁷.

If k_2 is greater than k_1 by an order of magnitude, then the observed values of k_1 would be expected to show definite trends due to the more rapid removal of O atoms by process (2). k_1 would be apparently smaller at long reaction times, and when the excess of O atoms was low. No such trends are observed in the values of k_1 obtained. This suggests that although $k_2 \geq k_1$, k_2 is not greater than k_1 by more than a factor of 2 or 3.

CHAPTER 4

THE REACTION OF HYDROGEN ATOMS WITH CHLORINE MONOXIDE

4.1 REACTION PRODUCTS

Reaction products were observed with total pressures between 0.14 and 0.30 torr, H atom pressures of 5×10^{-4} torr to 2.5×10^{-2} torr, Cl_2O pressures ranging from 5×10^{-4} torr to 2.5×10^{-2} torr, and reaction times varying from 0.5 msec to 100 msec. The relative proportions of H atoms and Cl_2O were varied from a 15 to 1 excess of atoms to a more than five-fold excess of Cl_2O .

The nature of the products after 100 msec reaction time was dependent upon whether Cl_2O or H atoms were in excess. With an excess of Cl_2O present, Cl_2 and O_2 were the major products and HCl and H_2O were minor ones. When an excess of H atoms was used, these positions were reversed and HCl and H_2O became the main products. All four products were formed in comparable amounts when the initial concentrations of H atoms and Cl_2O were nearly equal. The increase in peak height at mass 36 (HCl^+) due to the reaction, was always greater, by at least a factor of 4, than the increase at mass 18 (H_2O^+), and it is concluded that HCl was the more important of these two products. Similarly the increase at mass 70 (Cl_2^+) was about twice the increase at mass 32 (O_2^+) and it is apparent that more Cl_2 is formed than O_2 . These observations are as expected when it is considered that there are two Cl atoms

present for every O atom in the initial reactant Cl_2O .

The peaks at masses 86 (Cl_2O^+), 51 (ClO^+) and 52 (HOCl^+) were entirely absent after only a few milliseconds when H atoms were present in greater than two-fold excess. This implies that the reactions of H atoms with Cl_2O , ClO radicals and HOCl are all rapid. When Cl_2O was in excess, and with long reaction times, the peaks at masses 86 and 51 both decreased, while the peak at mass 52 simultaneously increased, when the discharge was activated. The decrease at mass 51 was proportionately smaller than the decrease at mass 86. At composition ratios near $\text{H}:\text{Cl}_2\text{O} = 1:1$, and with excess Cl_2O , the peak at mass 52 always increased when the discharge was turned on, even at the shortest reaction times attainable (ca. 0.5 msec). The mass 86 and mass 51 peaks always decreased at the shortest reaction times with either H atoms or Cl_2O in excess.

The contribution to the mass 51 peak due to unreacted Cl_2O could be calculated from observations of the relative peak heights of 51 (ClO^+) and 86 (Cl_2O^+) in the Cl_2O mass spectrum. When this contribution was subtracted from the mass 51 peak observed during reaction with excess Cl_2O present, the ratio of mass 51 (ClO^+) to mass 52 (HOCl^+) in the reaction products, after 100 msec, was typically 2:1. On the basis of the data shown in Table 4 it is expected that the mass spectrum of HOCl should contain the parent peak at mass 52 as its strongest feature.

Table 4

Fragment/Parent Ratios in Mass Spectra of Molecules
Similar to HOCl

Molecule	Bond	D_{298}^0 kcal. mole ⁻¹ (ref.81)	<u>Fragment Peak</u> <u>Parent Peak</u>	Relative Intensities Observed in Mass Spectrum	Ref.
Cl ₂ O	Cl-OC1	35	$\frac{ClO^+}{Cl_2O^+}$	$\frac{1.8}{1}$	Table 1
ClO ₂	O-ClO	58.8	$\frac{ClO^+}{ClO_2^+}$	$\frac{1}{3.2}$	70
H ₂ O	H-OH	119.2	$\frac{OH^+}{H_2O^+}$	$\frac{1}{4.7}$	(107 (This work
HOCl	H-OC1	98(±3)	$\frac{OC1^+}{HOCl^+}$?	-
	Cl-OH	60(±3)	$\frac{OH^+}{HOCl^+}$?	-

Note: Consider the sequence Cl₂O - ClO₂ - H₂O. Clearly, as D^0 increases so does the importance of the parent peak relative to the fragment peak. Since D^0 for H-OC1 lies between those of ClO₂ and H₂O so it might be expected that HOCl⁺:ClO⁺ will be between 3.2 and 4.7:1. Furthermore, HOCl gives ClO only by breaking the H-OC1 bond, while the other symmetrical molecules may all produce fragments by breaking either of two identical bonds. Thus HOCl⁺:ClO⁺ would be increased by a factor of 2 and it is almost certain therefore that

$$\begin{aligned}\frac{HOCl^+}{ClO^+} &= 6.4 \text{ to } 9.4 \\ &= 8 \pm 2\end{aligned}$$

The ratio of mass 52 to mass 51 is expected to be $8 \pm 2:1$. It follows therefore that since the mass 51 peak is the larger in the spectrum of products, that both ClO and HOCl are long-lived when Cl_2O is in excess relative to H atoms. Obviously not all of the ClO^+ can arise from HOCl . ClO was also found to be a long-lived product in the reaction of Cl_2O and oxygen atoms, and also, as will be shown later, in the reaction of Cl_2O with nitrogen atoms. In a typical experiment with $t = 100$ msec and with $\text{Cl}_2\text{O}:\text{H} = 2:1$ initially, the decrease at mass 86 when the discharge was turned on was 8.5×10^{-15} amperes, while the simultaneous increase at mass 52 was 7.5×10^{-15} amperes. (At the same time the product contribution to mass 51 was about 15×10^{-15} amperes.) Unfortunately it is not possible to obtain a figure for the absolute mass spectrometric sensitivity of HOCl , and this result cannot be converted to an estimate of the fraction of reacted Cl_2O that appears finally as HOCl .

A rather unexpected feature of the reaction was the observation that H_2 was consumed after long reaction times. When the discharge was activated in the absence of Cl_2O , the peak at mass 2 (H_2^+) typically decreased by about 15% as a consequence of dissociation of some of the molecular hydrogen to atomic hydrogen. However, with Cl_2O present ($\text{Cl}_2\text{O}:\text{H} = 1:1$) and with reaction time = 100 msec, the peak at mass 2 decreased by 35 to 40% upon discharging. This effect occurred both in the presence of excess H atoms and with

excess Cl_2O . With H atoms present in from three-fold to five-fold excess, the decrease at mass 2 in the presence of Cl_2O was between 2.0 and 2.5 times as large as that in the absence of Cl_2O . The effect was of about the same magnitude with $\text{H}:\text{Cl}_2\text{O} = 1:1$, and when a three-fold excess of Cl_2O was present the mass 2 decrease was about three times as large as when the Cl_2O was absent.

4.2 STOICHIOMETRY OF THE REACTION

The stoichiometry was measured with reaction times near 100 msec, with hydrogen atom pressures near 2×10^{-3} torr, and for $(\text{Cl}_2\text{O})_{\text{Total}} : (\text{Cl}_2\text{O})_{\text{Consumed}}$ ratios between 1.48:1 and 5.21:1. Table 5 shows the measurements made. The results show no significant dependence on the excess of Cl_2O present or on the total pressure at pressures near 0.15 torr. It was found that 1.11 ± 0.10 molecules of Cl_2O were consumed by each H atom (mean of 13 determinations).

4.3 THE RATE CONSTANT FOR THE PRIMARY REACTION

The same method was used as in the previous chapter, i.e., the primary rate constant was determined from the rate of consumption of Cl_2O in an excess of atomic hydrogen. The results are given in Table 6. Because of the rapidity of the reaction and the consequent need to use low atom concentrations, it was possible only to use relatively small excesses of H atoms.

Table 5

Stoichiometry of the H + Cl₂O ReactionReagent partial pressures in microns (10⁻³ torr).(1) (Argon) = 144; (H₂)_{discharge off} = 2.9; Time 101 msec.

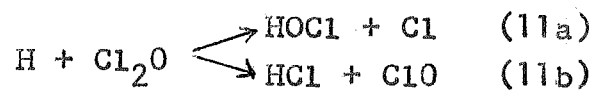
(H) _o	(Cl ₂ O) _o	Δ(Cl ₂ O)	$\frac{\Delta(\text{Cl}_2\text{O})}{(\text{H})_o}$	Relative excess* of Cl ₂ O
1.90	3.25	2.04	1.07 ± 0.12 [†]	1.59
1.77	3.27	1.91	1.08 ± 0.12	1.71
1.85	4.63	2.05	1.11 ± 0.12	2.26
1.50	3.85	1.62	1.08 ± 0.20	2.38
1.81	6.09	1.97	1.09 ± 0.12	3.09
1.60	6.30	1.85	1.16 ± 0.15	3.40
1.82	8.84	2.01	1.10 ± 0.10	4.40
Mean =			1.10 ± 0.12	

(2) (Argon) = 184; (H₂)_{discharge off} = 3.8; Time 113 msec.

(H) _o	(Cl ₂ O) _o	Δ(Cl ₂ O)	$\frac{\Delta(\text{Cl}_2\text{O})}{(\text{H})_o}$	Relative excess of Cl ₂ O
2.03	3.19	2.15	1.06 ± 0.13	1.48
2.00	4.15	2.27	1.14 ± 0.15	1.83
2.03	5.39	2.23	1.10 ± 0.15	2.41
2.00	5.82	2.17	1.08 ± 0.15	2.69
2.10	7.32	2.58	1.23 ± 0.15	2.83
2.03	11.71	2.25	1.11 ± 0.18	5.21
Mean =			1.12 ± 0.15	
Overall Mean =			1.11 ± 0.10	

*Relative excess of Cl₂O = ((Cl₂O)_o)/(Δ(Cl₂O))†Total estimated error in (Δ(Cl₂O))/((H)_o)

Table 6

Measurement of the Rate of the Primary Reactions

Reagent partial pressures given in microns (10^{-3} torr).

k_{11} = overall k for reactions (11a) + (11b).

(Argon)	(H ₂) discharge off	(H)	(Cl ₂ O) _o	(Cl ₂ O) _t	t msec	k_{11} cm ³ . mole ⁻¹ .sec ⁻¹
142	2	2.07	0.398	0.073	1.40	1.19 x 10 ¹³
"	"	"	0.450	0.184	0.724	1.19 "
"	"	"	0.403	0.108	0.995	1.30 "
143	1	1.03	0.349	0.179	1.00	1.33 "
"	"	"	0.343	0.147	1.91	0.90 "
"	"	"	0.370	0.084	3.19	1.03 "
"	"	"	0.358	0.152	1.59	1.10 "
"	"	"	0.339	0.203	0.729	1.38 "
150	1	0.887	0.326	0.166	1.18	1.32 "
"	"	"	0.333	0.109	2.17	1.28 "
"	"	"	0.318	0.048	3.64	1.36 "
"	"	"	0.315	0.201	0.803	1.26 "
"	"	"	0.328	0.156	1.46	1.20 "
140	1.5	1.29	0.266	0.080	1.55	1.23 "
"	"	"	0.223	0.100	1.05	1.16 "
"	"	"	0.248	0.139	0.599	1.46 "
"	"	"	0.234	0.047	2.10	1.21 "
"	"	"	0.226	0.102	0.824	1.46 "

(Table 6 contd.)

						69	
(Argon)	(H ₂) discharge off	(H)	(Cl ₂ O) _o	(Cl ₂ O) _t	t msec	k ₁₁ cm ³ . mole ⁻¹ .sec ⁻¹	
143	1	0.926	0.233	0.115	0.954	1.62 x 10 ¹³	
"	"	"	0.344	0.239	0.727	1.09	"
"	"	"	0.376	0.176	1.68	1.04	"
"	"	"	0.401	0.141	2.77	0.92	"
"	"	"	0.279	0.176	0.659	1.50	"
"	"	"	0.260	0.098	1.54	1.43	"
140	1.5	1.21	0.311	0.139	0.955	1.42	"
"	"	"	0.288	0.144	0.682	1.67	"
"	"	"	0.269	0.073	1.64	1.36	"
"	"	"	0.247	0.135	0.591	1.65	"
"	"	"	0.283	0.084	1.36	1.52	"
"	"	"	0.256	0.108	0.909	1.58	"

Mean k₁₁ = (1.31 ± 0.20) x 10¹³ cm³.mole⁻¹.sec⁻¹.

In spite of this, the values of k_{11} obtained show no obvious dependence on the size of the excess of H atoms which ranges from $\text{H}:\text{Cl}_2\text{O} = 2.3:1$ to $5.8:1$. The values also do not depend upon the reaction times at which the measurements were taken. It is concluded therefore that measured k_{11} values are not significantly affected by secondary reactions, and do in fact represent the primary rate constant.

The mean value found for k_{11} is $1.31 \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$, with a standard deviation of $0.20 \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$. The standard deviation in k_{11} is again about equal to the total estimated error of the measurements.

At the beginning of this investigation a large number of measurements of the primary rate constant were made without poisoning the walls of the reaction tube with phosphoric acid. The results of these measurements, which are not shown here, gave values for k_{11} which were lower and more scattered than those in Table 6. These values were in some cases a factor of 10 or more lower than the final mean value. Since phosphoric acid is an effective poison against wall recombination of chlorine atoms⁹³, it is believed that these low results were probably due to loss of H atoms between the titration gas jet and the Cl_2O jet. The H atoms could react with chlorine atoms adsorbed on the walls in the unpoisoned system.

Low values of k_{11} were also obtained if reactant partial pressures were too high, and if the H atoms were not in excess.

Obviously in these cases the apparent "primary" rate constant would be affected by slower secondary reactions. To ensure that the value of k_{11} obtained represented the initial process, reactant partial pressures were lowered (keeping at least a several-fold excess of atoms present), until the calculated k_{11} values no longer increased as the reactant pressures were decreased. Only these "plateau" values of k_{11} are shown in Table 6.

4.4 DISCUSSION

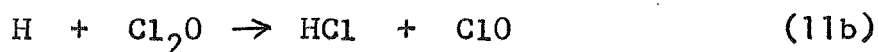
The hydrogen atom/ Cl_2O reaction system is too complex for a complete analysis of the mechanism to be made on the basis of the present measurements. Nevertheless, much useful information can be deduced on the basis of the product analysis and stoichiometry as follows.

HOCl was found to appear in the early stages of the reaction, under conditions where an appreciable proportion of the hydrogen atoms had still to react. This implies that the process

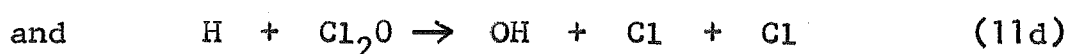
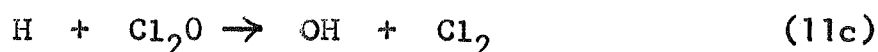


must be considered to be a significant primary reaction.

Using the listed heats of formation⁸¹ this reaction is found to be exothermic by $63.3 \pm 3 \text{ kcal.mole}^{-1}$, and it is possible that it could be rapid enough to explain the observed value of k_{11} . However, the alternative reaction path



is exothermic by $68.1 \text{ kcal.mole}^{-1}$. Steric considerations indicate that reaction (11b) should be the most probable primary process, and this reaction must almost certainly account for a significant, if not major, proportion of the primary reaction. The other possible primary processes



are assumed to be of negligible importance relative to reactions (11a) and (11b). Reaction (11c), although exothermic by $60.9 \text{ kcal.mole}^{-1}$, is a 4-centre reaction and is almost certainly several orders of magnitude slower than the observed primary rate. Reaction (11d) is exothermic ($3.0 \text{ kcal.mole}^{-1}$) but may be ruled out as it requires either the simultaneous breaking of two Cl-O bonds in the transition complex, or the formation of a very highly excited HOCl^* in reaction (11a).

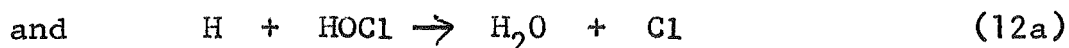
It is not possible on the basis of the present results to determine the relative rates of reactions (11a) and (11b). The observed primary rate constant, k_{11} , of $(1.31 \pm 0.20) \times 10^{13} \text{ cm}^3.\text{mole}^{-1}.\text{sec}^{-1}$ therefore represents the total rate for reactions (11a) + (11b).

Reaction (11a) is expected to be followed by the secondary processes

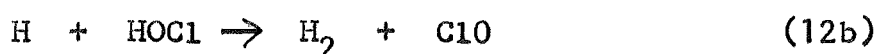


($k_3 > 4 \times 10^{11} \text{ cm}^3.\text{mole}^{-1}.\text{sec}^{-1}$, reference 22),



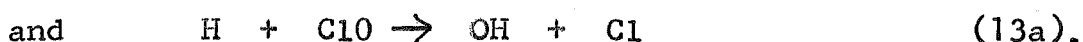


Reactions (12) and (12a) are exothermic by 43 and 59 kcal.mole⁻¹ respectively, and are both likely to be very fast. Together these reactions can account for the formation of HCl and H₂O, and the rapid disappearance of HOCl when H atoms are in excess. A third path for these reactants is

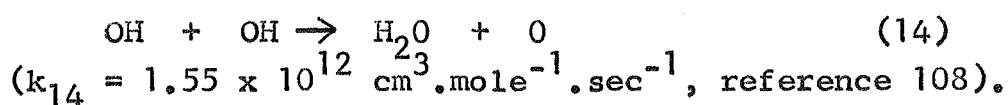


which is exothermic by 5.9 ± 3 kcal.mole⁻¹, and could also be quite rapid. However, if (12b) was important it might be expected that H₂ would be produced in the system. This is contrary to the observation that H₂ is consumed after a long reaction time, and other evidence suggests that this reaction probably proceeds in the reverse direction when Cl₂O is in excess. Reaction (12b) is therefore ruled out at this stage.

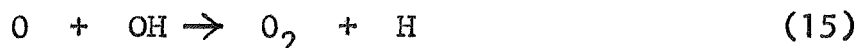
The important secondary reactions which follow reaction (11b) are expected to be



Once again there are two possible reaction paths which are almost equally exothermic (by 38.8 and 38.0 kcal.mole⁻¹ respectively), and both reactions are likely to be very fast. Reactions (11b) and (13) both produce HCl, and an alternative source of H₂O is now provided by the reaction

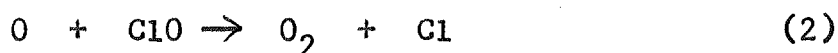


Another fate for OH, and a source of O_2 is provided by the reaction



where $k_{15} = (3 \pm 1) \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$, references 109 and 110.

An alternative means of producing O_2 is by way of the reaction

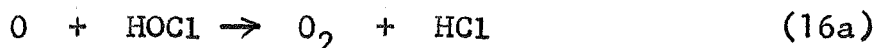


where $k_2 \geq 8 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (see chapter 3).

Other reactions of oxygen atoms which may occur are



($k_1 = 8.3 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$, this work, chapter 3),



($k_{18} = 3.1 \times 10^{10} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ at 298°K , ref. 88),

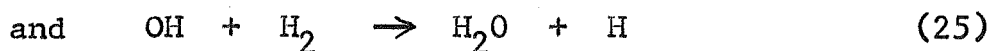
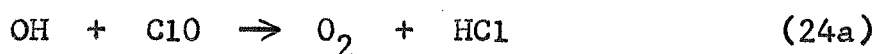
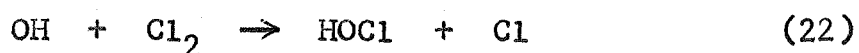


($k_{19} = 1.8 \times 10^6 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ at 298°K , ref. 111).

Reaction (1) will almost certainly be important when excess Cl_2O is present. Reaction (16) is just exothermic ($4 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$) and could be rapid; however, reaction (16a) is a 4-centre process and is probably unimportant. Reaction (17) is only just endothermic ($0.76 \text{ kcal} \cdot \text{mole}^{-1}$) and it is most probably slow,^{by} analogy with reactions (18) and (19), which are similar reactions involving O atoms and saturated molecules.

Reaction (18) is rather slow and is probably only of very minor importance in the present system, while reaction (19), and the reverse of (19), will both be quite negligible.

In addition to reactions (14) and (15) there are a number of other reactions which might remove OH. These are as follows:



where $k_{25} = 3.9 \times 10^9 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 108).

Reactions (20) and (21) are exothermic by 21 and 25 $\text{kcal} \cdot \text{mole}^{-1}$ respectively and could be important when Cl_2O is in excess.

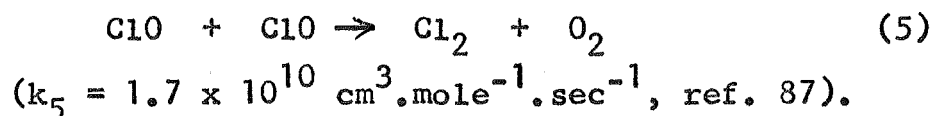
Reaction (22) is less likely as it is just exothermic ($2.4 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$), and reaction (22a) is probably unimportant as

it is a 4-centre process. Reaction (23), which is the difference of reactions (12) and (12a), is exothermic by 16 $\text{kcal} \cdot \text{mole}^{-1}$ and provides an alternative source of H_2O .

Reaction (24), which is the reverse of reaction (16), is probably endothermic ($4 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$), and consequently this reaction may be relatively slow. Reaction (24a) is another 4-centre process and can probably be neglected.

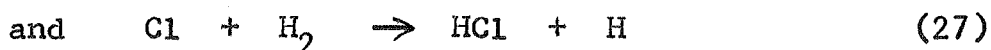
Reaction (25) is slow enough to be of marginal importance in the present reaction system, and certainly cannot be the process which consumes H_2 .

The process which was important in removing the ClO radicals in the O atom/ Cl_2 O reaction system, and which will probably be important after long times in this reaction scheme, is



It is worth noting here that reaction (5) is surprisingly rapid for a 4-centre process and that all other 4-centre processes mentioned in this discussion will almost certainly be much slower than reaction (5).

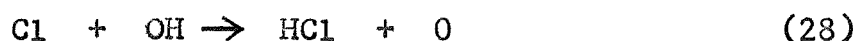
There are also a number of processes which remove chlorine atoms which must be considered in addition to reaction (3), namely



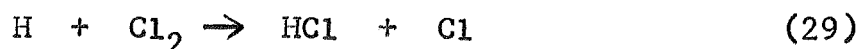
where $k_{27} = 1.4 \times 10^{10} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (ref. 112).

Reaction (26) is exothermic by $4.8 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$, and reaction (26a), which is the reverse of reaction (22), is endothermic by $2.4 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$. Either or both of these processes may operate early in the reaction scheme as both Cl

atoms and HOCl are formed by reaction (11a). Reaction (4) was rapid enough in the present flow apparatus to compete with reaction (3) in the O atom/Cl₂O reaction system, and will certainly operate to some extent in the reaction with H atoms. Reaction (27) is believed to be the process which is responsible for the observed consumption of H₂ after long reaction times, when H atoms are present in excess. The reverse of reaction (27), although some 3.3 times faster than the forward process at room temperature¹¹², will not be important in this system where H₂ concentrations are always much greater than those of the other species involved in reaction (27). In view of the rapidity of reaction (3), it seems likely that a different reaction must be responsible for H₂ consumption when Cl₂O is in excess. Two other reactions which could be significant are

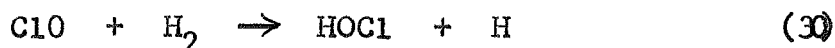


which is the reverse of (17) and is exothermic by 0.76 kcal.mole⁻¹, and



$$(k_{29} = 4 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}, \text{ refs 112, 113}).$$

The observed production of HOCl can be accounted for by reactions (11a), (21), (22) and (24), but the large consumption of H₂ when Cl₂O is in excess suggests that the reaction



must also be considered. This process is the reverse of reaction (12b) and is endothermic by 5.9 ± 3 kcal.mole⁻¹.

Although thermochemical considerations indicate that reaction (30) is not very rapid ($<10^{10} \text{ cm}^3.\text{mole}^{-1}.\text{sec}^{-1}$), it is possible that in view of the uncertainty in the listed value for ΔH_f° of HOCl (g), that the reaction could be less endothermic than calculated and therefore possibly fast enough to account for the observed removal of H_2 . Iredale and Edwards⁷² found evidence for reaction of ClO with H_2 , but they favoured the 4-centre process



Reaction (30a) is exothermic by $37 \text{ kcal.mole}^{-1}$ and could be significant if it were as fast as reaction (5), which is another 4-centre process. It is obvious then that there is some doubt as to which process removes H_2 when Cl_2O is in excess, and where reaction (27) is prevented from operating because of the rapidity of reaction (3). The reaction of ClO with H_2 could usefully be studied with a system of the type used by Clyne and Coxon⁸⁷, and such a study might confirm whether either or both of reactions (30) and (30a) are significant.

Two other reactions involving ClO radicals are

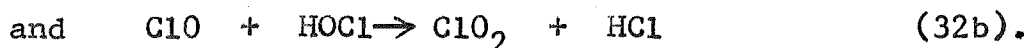
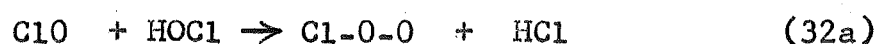
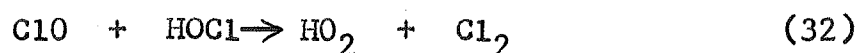
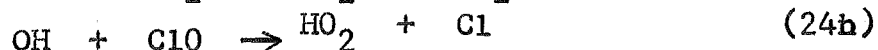
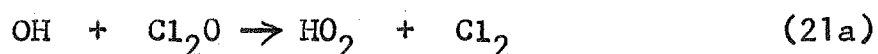
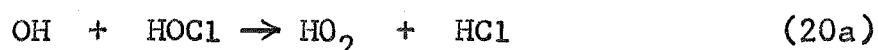
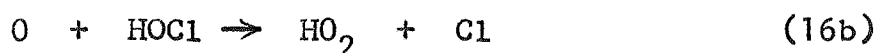


These could operate at long reaction times but both are unlikely because they are endothermic (7.2 and $4.8 \text{ kcal.mole}^{-1}$ respectively), and (31) is a 4-centre process.

The discussion of the mechanism of the H atom/ Cl_2O system

so far has included all possible reactions between species known or considered to be present. Termolecular processes have been excluded as even the most rapid of these will have negligible effect at the pressures used in the present study. Furthermore, all reactions which are endothermic by more than 9 or 10 kcal.mole⁻¹ have been ignored as these cannot possibly be rapid enough to influence the reaction system significantly. There are, however, several reactions involving ClO₂ and the radical species HO₂ and Cl-O-O which could participate.

These are



No evidence was found for the presence of mass peaks at 33 (HO₂⁺), 67 and 69 (ClO₂⁺) in the present study, and reactions involving these species have been assumed to be unimportant. Furthermore, all of the above reactions except (16b) and (24b) are 4-centre processes. Reactions involving the unknown species H-Cl-O have also been ignored in the above discussion. The existence of this species seems highly unlikely, but if it were formed it could not be distinguished from HOCl in the mass spectrometer.

The observed stoichiometry, $\Delta(\text{Cl}_2\text{O})/\Delta(\text{H}) = 1.11 \pm 0.10$, can be explained by reaction schemes beginning with either of the primary steps (11a) and (11b), if suitable assumptions are made as to the relative importance of the various secondary steps. The main point of difficulty in such schemes is the effect of the consumption of H_2 after long reaction times. If this occurs by reactions (27) or (30) atomic hydrogen is regenerated, and a chain is set up which tends to increase the consumption of Cl_2O per initial H atom. If H_2 is consumed by reaction (30a), Cl_2O will be consumed by O atoms by way of reactions (14) and (1). The amount of H_2 consumed indicates that at least half of the original number of hydrogen atoms would be regenerated if the reactions (27) or (30) were involved, or alternatively, half of this amount of atomic oxygen would be produced by reaction (14) if reaction (30a) alone was involved. The observed stoichiometry of 1.11 ± 0.10 appears to favour reaction (30a), but the difference is marginal because of the large number of species besides Cl_2O which are able to remove the additional atomic hydrogen from the system.

The above scheme of reactions is able to account for the various products and intermediates observed, and is sufficiently flexible for the observed stoichiometry to be accounted for, at least semi-quantitatively. It is obvious, however, that the system is very complex and there are many possible reactions

for which kinetic data is unavailable. For this reason further quantitative analysis of the H atom/ Cl_2O reaction system is not possible.

CHAPTER 5

THE REACTION OF NITROGEN ATOMS WITH CHLORINE MONOXIDE

5.1 REACTION PRODUCTS

Reaction products were observed at both long and short reaction times, with a molecular nitrogen pressure of 0.310 torr, and an atomic nitrogen partial pressure of 3×10^{-3} torr. The Cl_2O pressure was varied from slightly less than that of the N atoms to more than 100 times the N atom pressure.

Large increases in peak height at mass 70 (Cl_2^+) and at mass 32 (O_2^+) were observed 100 msec after mixing of reactants when the discharge was activated. These correspond to the stable reaction products chlorine and oxygen. As was the case in the hydrogen atom/ Cl_2O reaction system, the increase at mass 70 was consistently some 2 or 3 times larger than the increase at mass 32. This indicates that chlorine is probably formed in greater quantities than is oxygen, which is to be expected from the initial proportions of these two elements in Cl_2O .

No change was detectable in the mass 28 (N_2^+) peak after long reaction times when the discharge was activated in the presence of Cl_2O . With Cl_2O absent, it was possible to detect only a very slight decrease at mass 28 on activating the discharge. This was due to the large excess of N_2 present relative to the N atom concentration. The net result was that

a slight increase was observed at mass 28 due to reaction products. However, the increase was barely above the noise level of the relatively large mass 28 signal. It seems almost certain, on the basis of this observation, that molecular nitrogen is formed in the reaction. This was confirmed by the failure to detect any other nitrogen-containing compounds as stable products after long reaction times. The nitrogen atoms are therefore ultimately recombined as a result of the reaction, the Cl_2O acting as a catalyst.

With initial pressures of Cl_2O and atomic nitrogen both of 3×10^{-3} torr, and a reaction time of 100 msec, the peak at mass 51 (ClO^+) fell to about 50% of its initial value when the discharge was activated. At the same time the peak at mass 86 (Cl_2O^+) fell to much less than 5% of its initial value. This indicates that once again the ClO radical is a relatively long-lived intermediate in the reaction system.

No definite increase was observed at mass 49 (NCl^+), such as would be attributable to the formation of NCl , when the discharge was activated, even at very short reaction times. A similar negative result was obtained for mass 30 (NO^+), with both small and large (up to 100-fold) excesses of Cl_2O present, and with short and long reaction times. (At both of these mass numbers a small increase was observed when the discharge was activated in the absence of Cl_2O . The increase when Cl_2O was present was in both cases slightly smaller than that obtained

with Cl_2O absent. These increases are attributable either to products of interaction of N atoms with the reaction vessel wall coating, or to secondary reactions occurring inside the mass spectrometer ion source.) The negative result obtained for NO implies that it is definitely not a product of the reaction since the mass spectrometric sensitivity for NO is known to be high and therefore even very small amounts of NO would have been readily detectable. Furthermore, excesses of Cl_2O would have prevented the consumption of any NO formed by reaction with N atoms. The failure to detect NCl does not necessarily rule out the presence of this species as an intermediate. The NCl radical may have been destroyed very efficiently by interaction with the sampling leak or the walls of the ionization chamber of the mass spectrometer. Alternatively, the steady state concentration of NCl was probably very low and also the mass spectrometric sensitivity for this species may be quite low. A low steady state concentration of NCl would imply that it is consumed by very rapid reactions.

5.2 STOICHIOMETRY OF THE REACTION

Measurements of the overall reaction stoichiometry are shown in Table 7. The relative excess of Cl_2O present ($= (\text{Cl}_2\text{O})_{\text{Total}} : (\text{Cl}_2\text{O})_{\text{Consumed}}$) ranged from 1.5:1 to 5.5:1 with N atom pressures between 1.8×10^{-3} and 3.0×10^{-3} torr.

Table 7

Stoichiometry of the N + Cl₂O ReactionReagent partial pressures in microns (10⁻³ torr).(1) (N₂) = 330; Time 100 msec.

(N) _o	(Cl ₂ O) _o	Δ(Cl ₂ O)	$\frac{\Delta(\text{Cl}_2\text{O})}{(\text{N})_o}$	Relative excess* of Cl ₂ O
2.34	3.30	2.16	0.92 ± 0.12 ⁺	1.53
2.45	3.54	2.18	0.89 ± 0.15	1.63
2.00	3.17	1.82	0.91 ± 0.15	1.74
2.34	4.23	2.12	0.91 ± 0.15	2.00
2.46	4.52	2.17	0.88 ± 0.12	2.08
2.10	5.15	2.06	0.98 ± 0.15	2.50
2.16	7.01	2.08	0.96 ± 0.15	3.38
2.51	10.70	2.25	0.90 ± 0.10	4.76
2.70	14.25	2.60	0.96 ± 0.25	5.49
Mean =			0.92 ± 0.10	

(2) (N₂) = 313; Time 114 msec.

(N) _o	(Cl ₂ O) _o	Δ(Cl ₂ O)	$\frac{\Delta(\text{Cl}_2\text{O})}{(\text{N})_o}$	Relative excess of Cl ₂ O
2.63	6.04	2.42	0.92 ± 0.20	2.50
3.13	8.12	3.03	0.97 ± 0.25	2.68
3.13	13.21	3.03	0.97 ± 0.20	4.36
Mean =			0.95 ± 0.20	
Overall Mean =			0.93 ± 0.10	

*Relative excess of Cl₂O = ((Cl₂O)_o)/(Δ(Cl₂O))⁺Total estimated error in (Δ(Cl₂O))/(N)_o

Measurements were taken around 100 msec reaction time with total pressures of 0.313 and 0.330 torr. The mean of 12 determinations of $\Delta(\text{Cl}_2\text{O})/\Delta(\text{N})$ is 0.93 ± 0.10 . There is no trend apparent in the stoichiometry as the composition is varied, and there is no obvious dependence on the total pressure in the small pressure range used.

5.3 THE RATE CONSTANT FOR THE PRIMARY REACTION

The rate constant was determined by measuring the rate of disappearance of Cl_2O in the presence of a large stoichiometric excess of N atoms, and using short reaction times. The results are given in Table 8. It is found that there is a marked trend towards higher values for the primary rate constant at lower N: Cl_2O ratios. There is also a less definite trend towards higher rate constants at longer reaction times. The most likely explanation of these trends is that Cl_2O is involved in a secondary reaction which is somewhat faster than the primary reaction between N atoms and Cl_2O . It follows that the most reliable values for the rate constant will be those obtained with the largest N: Cl_2O ratios. The mean of all the rate constant values given in Table 8 (except the two extreme values which are marked with asterisks) is $1.04 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$. The mean of the values obtained using N: Cl_2O greater than 10:1, where the trend has largely disappeared, is $9.1 \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ with a standard deviation of $1.5 \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$.

Table 8

Measurement of the Rate of the Primary Reaction

Reagent partial pressures given in microns (10^{-3} torr).

(N_2)	$(\text{N})_0$	$(\text{Cl}_2\text{O})_0$	$(\text{Cl}_2\text{O})_t$	t msec	$\frac{(\text{N})_0}{(\text{Cl}_2\text{O})_0}$	k_{33}	$\text{cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$
155	3.90	0.263	0.169	2.22	14.8	9.6×10^{11}	
"	"	0.247	0.114	3.73	15.8	10.0	"
"	"	0.227	0.055	5.61	17.2	12.3	"
"	"	0.227	0.110	3.18	17.2	11.0	"
"	"	0.206	0.144	1.66	18.9	10.3	"
"	"	0.176	0.098	2.70	22.2	10.4	"
174	5.00	0.192	0.117	2.34	26.1	7.9	"
"	"	0.175	0.071	4.14	28.6	8.2	"
"	"	0.179	0.098	2.73	27.9	8.3	"
"	"	0.260	0.124	3.54	19.2	7.8	"
"	"	0.238	0.163	1.88	21.0	7.6	"
"	"	0.252	0.126	3.19	19.8	8.2	"
154	4.26	0.375	0.189	3.41	11.4	9.0	"
"	"	0.337	0.088	5.16	12.7	11.8	"
"	"	0.320	0.205	2.54	13.3	7.8	"
"	"	0.339	0.148	3.95	12.6	9.4	"
"	"	0.339	0.084	5.62	12.6	11.3	"
"	"	0.323	0.248	1.67	13.2	7.1	"
"	"	0.353	0.200	3.11	12.1	8.2	"
181	4.72	0.376	0.225	2.82	12.6	7.3	"

(Table 8 contd)

(N ₂)	(N) _o	(Cl ₂ O) _o	(Cl ₂ O) _t	t msec	$\frac{(N)_o}{(Cl_2O)_o}$	k ₃₃	cm ³ .mole ⁻¹ . sec ⁻¹
181	4.72	0.333	0.118	4.12	14.2	10.1 x 10 ¹¹	
"	"	0.385	0.199	3.33	12.3	7.9	"
"	"	0.427	0.204	3.71	11.1	8.0	"
"	"	0.417	0.308	2.17	11.3	5.5	" *
133	2.78	0.343	0.247	1.91	8.1	11.6	"
"	"	0.405	0.200	4.08	6.9	12.1	"
"	"	0.381	0.116	6.49	7.3	13.0	"
"	"	0.384	0.054	8.53	7.2	16.7	"
"	"	0.410	0.161	5.08	6.8	12.9	"
"	"	0.340	0.185	3.63	8.2	11.5	"
"	"	0.342	0.216	2.72	8.1	11.5	"
138	2.40	0.395	0.247	3.63	6.1	10.3	"
"	"	0.274	0.138	5.56	8.8	9.9	"
"	"	0.259	0.061	8.18	9.3	14.4	"
"	1.54	0.270	0.202	4.43	5.7	8.1	"
"	"	0.279	0.176	7.49	5.5	7.7	"
140	2.17	0.333	0.129	5.87	6.5	14.6	"
"	"	0.311	0.158	4.15	7.0	14.5	"
"	"	0.284	0.195	2.52	7.6	13.0	"
"	"	0.283	0.135	4.99	7.7	13.1	"
"	"	0.346	0.054	8.15	6.3	21.3	" *
"	"	0.320	0.186	3.91	6.8	12.3	"
"	"	0.300	0.101	6.79	7.2	14.5	"

Mean k₃₃ = 1.04 x 10¹² cm³.mole⁻¹.sec⁻¹

Mean k₃₃ with $\frac{(N)_o}{(Cl_2O)_o} > 10 = (9.1 \pm 1.5) \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$

This second mean value has been taken as representing the rate constant for the primary reaction, k_{33} .

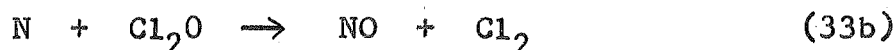
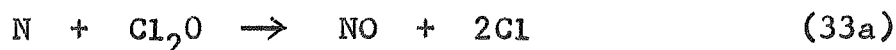
5.4 DISCUSSION

The primary reaction in this system is undoubtedly



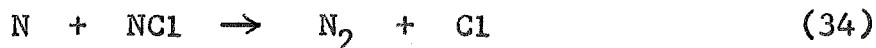
where $k_{33} = (9.1 \pm 1.5) \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (this work).

The alternative primary steps



may all be ruled out as unimportant in this system. The failure to detect NO rules out reactions (33a) and (33b), apart from any other considerations. Both the species N-O-Cl and N-Cl-O are unknown (Nitrosyl chloride has the structure O-N-Cl) and therefore reactions (33c) and (33d) are considered unlikely. The species N-O-Cl would, if present, produce a peak at mass 30 (NO^+), and the absence of this peak is further evidence against reaction (33c).

The primary reaction (33) will be almost certainly followed by the secondary reactions:



where $k_1 = 8.3 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (this work, chapter 3),



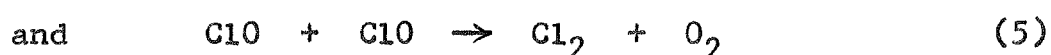
where $k_2 \geq 8 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (this work, chapter 3),



where $k_3 > 4 \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 22),



(likely to be slow with poisoned walls⁹³)



where $k_5 = 1.7 \times 10^{10} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (reference 87).

It might be expected that the alternative reaction



would be important in removing ClO radicals from the system (reaction (35a) is exothermic by $86.7 \text{ kcal} \cdot \text{mole}^{-1}$). However, this reaction is ruled out by the absence of any peak at mass 30 (NO^+) in the reaction products formed with a large excess of Cl_2O initially present. The excess of Cl_2O would have minimized the possibility of rapid consumption of NO by reaction with N atoms. Furthermore, products of any subsequent reaction of NO in the absence of N atoms, for example NOCl or NO_2 , would have been detected with certainty because of their contributions to the peak at mass 30.

Other reactions which can be shown to be unimportant in the present reaction system are as follows.

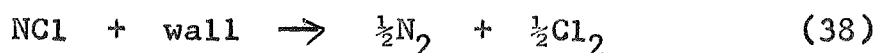


Reaction (36), which is the reverse of reaction (35), may

possibly be rapid. However, it will be shown below that reaction (35) is required to be very fast in order to explain satisfactorily the experimental observations. In the present reaction system the concentrations of N atoms and ClO will always be much higher than those of O atoms and NCl, so that reaction (35) may be expected to predominate. O atoms and NCl are both removed by several very rapid reactions, viz. (1), (2) and (34), and their steady state concentrations will consequently be very low. Reaction (36a) is ruled out by the absence of NO in the reaction products. The reaction



is endothermic by at least 6 kcal.mole⁻¹ (using the value for D° for NCl which is derived below) and is therefore unlikely to operate in the present reaction system. All the possible reactions between N, O or Cl atoms and the diatomic species N₂, O₂ and Cl₂ are too slow to be important. Finally, the possibility of destruction of NCl at the wall by



is considered unlikely. The analogous process for NI has been shown to be unimportant, relative to the gas phase destruction of NI by N atoms, in the reaction of atomic nitrogen with I₂⁹⁰. NBr is also apparently not destroyed at the walls in a pyrex vessel¹¹⁴.

The observed properties of the N atom/Cl₂O reaction system can be interpreted satisfactorily in terms of reactions (33), (34), (35), and (1) to (5) inclusive. The rate constants

for reactions (34) and (35) are unknown, but both are likely to be very rapid. The production of O atoms by reaction (35) permits the subsequent reaction (1), which is now identified as the fast secondary process that consumes Cl_2O and produces the observed trends in the values of k_{33} , the primary rate constant. It is also possible to explain the fast secondary consumption of Cl_2O in terms of reaction (3), for which the rate constant is known only as a lower limit. However, reaction (1), which is certainly known to be nearly 10 times as fast as reaction (33), must be considered the more important. Whichever of the two reactions (34) or (35) leads ultimately to the consumption of more Cl_2O , it must have a rate constant of at least an order of magnitude greater than k_{33} to account for the observed variation in k_{33} when the $\text{N}:\text{Cl}_2\text{O}$ ratio is varied. More generally it may be stated that $(k_{34} + k_{35}) \geq 10^{13} \text{ cm}^3.\text{mole}^{-1}.\text{sec}^{-1}$, with k_{34} and k_{35} each $\geq 10^{12} \text{ cm}^3.\text{mole}^{-1}.\text{sec}^{-1}$.

In order for reaction (35) to be fast it must be exothermic, or at least thermoneutral. The dissociation energy of ClO is $64.3 \text{ kcal.mole}^{-1}$ at 298°K ,⁸¹ so that on the basis of the above evidence that reaction (35) is rapid, it may be deduced that the dissociation energy for NCl at 298°K is $\geq 64 \text{ kcal.mole}^{-1}$. Vedeneyev et al.¹¹⁵ list an estimated heat of formation for NCl which leads to a dissociation energy of about $62 \text{ kcal.mole}^{-1}$ at 298°K , but the limits of error on this value are probably rather large.

Finally, the stoichiometry of the reaction may be considered. The sequence of reactions (33) to (35) and (1) to (3) constitutes a branched chain which may be terminated by either reaction (4) or reaction (5). For the secondary reactions it may be noted that every reaction of a nitrogen atom with ClO yields an oxygen atom, which can subsequently react with either Cl_2O or ClO . If the O atom reacts with ClO it generates a chlorine atom, which can then react with Cl_2O unless lost by recombination on the wall. Similarly, reaction of a nitrogen atom with NCl yields a chlorine atom, which may also react with Cl_2O unless lost by wall recombination. Thus the above reaction scheme predicts that the overall stoichiometry, $\Delta(\text{Cl}_2\text{O})/\Delta(\text{N})$, should be $= 1$ if there is negligible wall recombination of the chlorine atoms. The experimentally observed value of $\Delta(\text{Cl}_2\text{O})/\Delta(\text{N}) = 0.93 \pm 0.10$ indicates that a small proportion of the chlorine atoms present in the system are in fact removed by recombination at the walls, rather than by reaction (3).

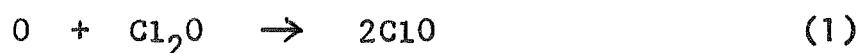
CHAPTER 6

SUMMARY AND CONCLUSIONS

6.1 SUMMARY OF RESULTS

(i) Rate Constants

The rate constant for each of the primary reactions of oxygen atoms, hydrogen atoms and nitrogen atoms with chlorine monoxide has been determined by direct measurement of the rates of disappearance of Cl_2O in the presence of excess concentrations of atoms. These rate constants are as follows.



$$k_1 = (8.3 \pm 1.4) \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K}.$$



$$k_{11} = k_{11a} + k_{11b}$$

$$= (1.31 \pm 0.20) \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K}.$$

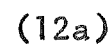


$$k_{33} = (9.1 \pm 1.5) \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K}.$$

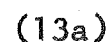
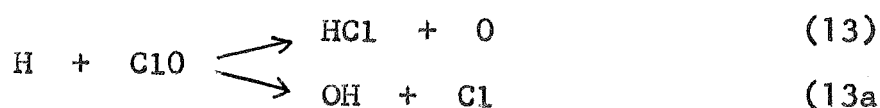
Approximate values for the rate constants of some of the more important secondary processes occurring in the reactions of Cl_2O with atoms have been deduced from the experimental data as follows.



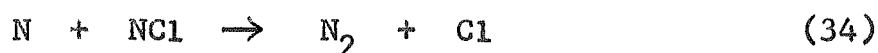
$$k_2 \geq 8 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K.}$$



$$(k_{12} + k_{12a}) > 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ and probably} \\ \sim 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K.}$$



$$(k_{13} + k_{13a}) > 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ and probably} \\ \sim 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K.}$$



$$k_{34} + k_{35} \geq 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ with} \\ k_{34} \text{ and } k_{35} \text{ both } \geq 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{ at } 298^\circ\text{K.}$$

(ii) Reaction Stoichiometry Measurements

In the reaction of oxygen atoms with Cl_2O , the number of molecules of Cl_2O consumed after 100 msec by each oxygen atom present initially was 0.72 ± 0.15 , at a total pressure of 0.24 torr, and 0.88 ± 0.15 , at a total pressure of 0.32 torr.

In the reaction of hydrogen atoms with Cl_2O , each hydrogen atom initially present consumed 1.11 ± 0.10 molecules of Cl_2O after 100 msec reaction time at total pressures near 0.15 torr.

In the reaction of nitrogen atoms with Cl_2O , each nitrogen

atom initially present consumed 0.93 ± 0.10 molecules of Cl_2O after 100 msec reaction time at total pressures near 0.32 torr.

(iii) Reaction Products

The reaction of Cl_2O with oxygen atoms produced molecular oxygen and chlorine as stable products, while ClO radicals were present as a long-lived intermediate species for over 100 msec of reaction time at the reactant pressures used.

The reaction of hydrogen atoms with Cl_2O produced O_2 , Cl_2 , H_2O and HCl as stable products, the relative proportions of these depending upon the initial proportions of reactants. When an excess of Cl_2O was initially present HOCl was an important product and ClO was a long-lived intermediate species. Significant amounts of molecular hydrogen were consumed by secondary reactions.

The reaction of Cl_2O and nitrogen atoms produced Cl_2 , O_2 and N_2 as final reaction products. No nitric oxide or other oxides of nitrogen were present as products or intermediates. The ClO radical was once again found as a long-lived intermediate which persisted for over 100 msec after mixing of reactants. The presence of the reactive intermediate species NCl is postulated in order to explain the experimental observations; however, no direct observation of this radical was possible. A lower limit for the dissociation energy of NCl at 298°K of $64 \text{ kcal.mole}^{-1}$ was deduced from the reaction mechanism.

6.2 GENERAL OBSERVATIONS ON THE REACTION SYSTEMS STUDIED

It is apparent that Cl_2O shows high reactivity towards each of the atoms used in the present study. All of the primary rate constants are of the order of 10^{12} to $10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ at 298°K , which indicates that the activation energies for the primary processes must all be low, i.e. less than about $5 \text{ kcal} \cdot \text{mole}^{-1}$ for the N atom reaction, and less than 2 or 3 $\text{kcal} \cdot \text{mole}^{-1}$ for the O and H atom reactions.

Molecular oxygen and chlorine appear as final products in all three reaction systems, as they also do in the photochemical and thermal decompositions of chlorine monoxide. The hydrogen atom/ Cl_2O reaction system is the most complex and gives by far the greatest variety of products. The nitrogen atom reaction is unique in that the initial reactant atoms do not appear in any of the final stable products but are merely recombined as a result of the overall reaction. This is somewhat surprising in view of the stability of molecules such as NO, NO_2 , nitrosyl chloride (ONCl), etc.

The ClO radical was detected directly as a long-lived intermediate in all the reaction systems when Cl_2O was in excess. It is apparent that in the reactions studied in this work this radical plays an important role, as indeed it does in most other reactions of chlorine monoxide and chlorine dioxide. It may also be noted that the ClO radical undergoes rapid reactions ($k \sim 10^{12}$ to $10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$) with O atoms, H atoms, and N atoms.

Another interesting feature is that in all cases the overall reaction stoichiometry is somewhere near 1:1, molecules of Cl_2O consumed: initial atoms present. That this is so is due to the rapidity of the reactions of O atoms and Cl atoms with Cl_2O . In the reactions of O atoms and N atoms with Cl_2O , wherever one of the original atoms does not react with a Cl_2O molecule, but another species, it generates either an O atom or a Cl atom which continues the reaction chain and is then capable of rapid reaction with Cl_2O . Thus in these cases the stoichiometry eventually becomes 1:1, $\Delta(\text{Cl}_2\text{O})/\Delta(\text{atoms})$, with some reduction in the amount of Cl_2O consumed per initial atom because of chain termination by wall recombination of chlorine atoms. The hydrogen atom/ Cl_2O reaction system is similar, but in this case there are a number of chain branching steps possible. Also there is the primary reaction (11a) where a hydrogen atom and a Cl_2O molecule react to produce a Cl atom which can then consume a further Cl_2O molecule. In contrast, both the O atom and N atom primary reactions produce only species which are relatively unreactive towards Cl_2O . Thus it is expected that the stoichiometry in the H atom/ Cl_2O system, $\Delta(\text{Cl}_2\text{O})/\Delta(\text{H})$, will be greater than 1, as is in fact observed.

6.3 COMPARISON OF RATES OF ATOM-HALOGEN REACTIONS

It is interesting to compare the rates of the primary reactions of O, H and N atoms with various halogens, and to include in this comparison the values obtained in this work, i.e. Cl_2O is considered as a pseudo-halogen. Table 9 lists the relevant information, where it is available.

It is obvious that for all the halogens the primary rate constants decrease in the order H atoms > O atoms > N atoms. The second and less clearly defined trend is that the rate constants for a particular atom increase as the halogen bond strength decreases, i.e. rate for $\text{Cl}_2\text{O} > \text{I}_2 > \text{Br}_2 > \text{Cl}_2$, with one or two exceptions.

6.4 SUGGESTIONS FOR FUTURE WORK

A reaction which appears as an important process in each of the systems studied here is



The value of the rate constant k_3 is known only as a lower limit of $4 \times 10^{11} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (ref. 22). Clearly, it would be useful to have a more definite estimate of k_3 and such a determination is suggested here as a possible future line of research. However, it may not be possible to use a system of the present type to carry out such a study, for several reasons. Firstly, considerable difficulties will be encountered in handling chlorine or chlorine/argon mixtures, as compared with O_2 , H_2 or N_2 .

Table 9Primary Rates of Atom-Halogen Reactions

(Rate constants are in $\text{cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ and all refer to $298^\circ\text{K}.$)

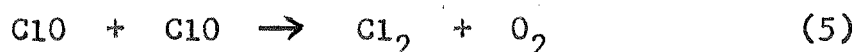
Rates of primary atom-halogen reactions				Bond dissociation energy in halogen in $\text{kcal} \cdot \text{mole}^{-1}$ at 298°K
	N atoms	O atoms	H atoms	
Cl_2	1.9×10^8	3.1×10^{10}	4.3×10^{12}	57.9
Br_2	2.2×10^9	$> 10^{10}$	3×10^{13}	46.1
I_2	3.4×10^{10}	-	1.5×10^{13}	36.1
Cl_2O	9.1×10^{11}	8.3×10^{12}	1.3×10^{13}	35.0 ($\text{Cl}-\text{OCl}$)

<u>References:</u>	$\text{N} + \text{Cl}_2$	} ref. 90	$\text{H} + \text{Cl}_2$	refs 112,113
	$\text{N} + \text{Br}_2$		$\text{H} + \text{Br}_2$	refs 117,118
	$\text{N} + \text{I}_2$	ref. 116	$\text{H} + \text{I}_2$	ref. 117
	$\text{O} + \text{Cl}_2$	ref. 88	All Cl_2O values - this work	
	$\text{O} + \text{Br}_2$	refs 45,88	Bond energies	ref. 115

Although chlorine is readily dissociated to atoms in a discharge of the type used here, the rate of decay of chlorine atoms in the present flow system has been shown to be appreciable. This difficulty could be overcome by regular and frequent poisoning of the reaction tube walls⁹³ and by using a shorter reaction tube. In addition, there will probably be considerable contamination of the stainless steel surfaces inside the mass spectrometer ion chamber by the relatively large amounts of Cl_2 that would be used in such a study. Finally, it would be necessary to find a suitable means of titrating Cl atoms. Nitrosyl chloride has been used for the titration of Cl atoms⁹³, but recent work in this laboratory has shown that NOCl has an extremely small parent peak in its mass spectrum¹¹⁹. For this reason, NOCl cannot readily be used as a titrant for low Cl atom concentrations if a mass spectrometer is to be used as a detector. Alternatively, the titration end point can be determined photometrically, but this method may be limited to Cl atom pressures which are too high for satisfactory kinetic measurements on the rapid reaction (3).

Some of the reactions of ClO radicals which are of interest as secondary processes in this work may usefully be studied in a system similar to that used by Clyne and Coxon⁸⁷. These workers generate ClO radicals by adding a stoichiometric amount of ClO_2 to a stream of Cl atoms which then under the rapid reaction $\text{Cl} + \text{ClO}_2 \rightarrow 2\text{ClO}$ (39).

Both the reactions of Cl atoms and ClO_2 with ClO radicals are slow and the ClO radicals once generated in this way are not removed except by reaction (5), i.e.

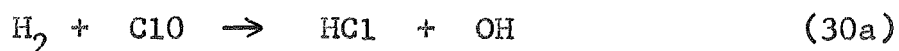


where $k_5 = 1.7 \times 10^{10} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ (ref. 87).

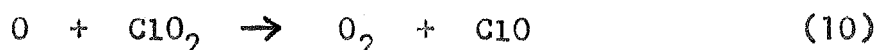
It will be possible to add other reactants a short distance downstream from the point where ClO_2 is added, and to follow subsequently the reactions of these other reactants with ClO radicals which themselves decay only relatively slowly.

The present type of mass spectrometric system would probably be particularly suited to studying such reactions if modifications were made to the reaction flow system.

Examples of these reactions which have been encountered in the present study are



Finally, the reactions of O atoms, H atoms and N atoms with ClO_2 could all be studied without too much difficulty in the present apparatus. The primary reaction with O atoms



has been shown to be very rapid, $k_{10} > 2.4 \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ at 298°K (ref. 87). It is likely that the reactions

with H atoms and N atoms are also very fast. The mass spectrum of ClO_2 has been reported⁷⁰ and it contains relatively large ClO_2^+ parent peaks. For this reason no major difficulties should be encountered in using the present mass spectrometer to monitor the low ClO_2 concentrations which would be required in kinetic studies of the above reactions. The main difficulty in such a study is likely to arise from the highly explosive nature of ClO_2 ¹²⁰.

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